ANALYTICAL CHEMISTRY

BASED ON THE TEXT OF F. P. TREADWELL

REVISED AND ENLARGED BY WILLIAM T. HALL

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Analytical Chemistry

BASED ON THE GERMAN TEXT

OF

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Late Professor of Analytical Chemistry at the Polytechnic Institute of Zurich

TRANSLATED AND REVISED

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VOLUME I

QUALITATIVE ANALYSIS

NINTH ENGLISH EDITION

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PREFACE TO THE NINTH EDITION

Many changes have been made in this revision. Part I, which deals with the principles upon which analytical chemistry is based, has been largely rewritten to make it correspond more closely to modern chemical theory. Part II, which treats of the reactions of cations, has been rearranged so that the order of treatment may correspond to the sequence in which the laboratory tests are made. In previous editions, the reactions of the alkali cations were discussed first and the cations of the silver group, which constitute Group I of the analytical procedure, were considered last. Since this has caused some confusion in the minds of beginners, it is believed that the new arrangement will be found more convenient.

Considerable new material has been introduced throughout the book. The description of properties of the elements has been amplified and many new tests described with special attention to drop reactions. A procedure for semi-microchemical analysis has been introduced. Since it was the earnest desire of the publishers not to increase the price of the book, the introduction of the new material made it necessary to discard considerable portions of the former text. Thus, for the analysis of each group of cations, a single scheme of analysis is now recommended which will, it is hoped, make it easier for the beginner. The excellent scheme of Noyes and Bray for the analysis of the rare and common metals has been omitted with regret. The procedure is so long that few students find time to follow it throughout and it has been found better to refer them to the original text of Noyes and Bray where greater attention is paid to the necessary details of manipulation and considerable information is given about tests that were made in developing the scheme. In some cases, as in the analysis of the platinum metals and in the tests for the earths and earth acids, the scheme of Noyes and Bray no longer corresponds to the best modern practice.

The section on spectroscopy has also been shortened with regret. The technique of spectroscopic analysis has developed so remarkably during recent years that it is now beyond the scope of this book to give adequate treatment to this important method of analysis. The syllabus of the course in qualitative analysis given at the Massachusetts Institute of Technology has also been omitted, partly to save space and

partly because of changes made from year to year in the actual method of instruction.

The labor of proofreading has been lightened very considerably by conscientious work on the part of my associates Professor Stephen G. Simpson and Mr. Robert M. Sherman, Jr., who have offered many valuable suggestions.

WILLIAM T. HALL

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
April, 1937

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Qualitative Analysis

PART I. GENERAL PRINCIPLES

Analytical chemistry includes all those operations which are performed in order to determine the constituents of a chemical compound (or a mixture of chemical compounds). Analytical chemistry is subdivided into qualitative analysis and quantitative analysis.

Qualitative analysis treats of the methods for determining the nature of the constituents of a substance. Quantitative analysis treats of the methods for determining *in what proportion* the constituents are present in any compound or mixture of compounds.

Qualitative tests, however, can show the approximate content of constituents by comparing the result of a test with that obtained with a known quantity of pure material. Colorimetric tests which are often suitable for determining small quantities of a constituent, and tests to determine purity, are almost always made with reactions used in qualitative analysis.

In order to recognize a substance we change it, usually with the help of another substance of known nature, into a new compound which possesses distinctive properties. This transformation we call a *chemical reaction;* and the substance by means of which the reaction is brought about, the *reagent.*

We distinguish between reactions in the *wet way* and reactions in the *dry way.*

I. Reactions in the Wet Way

For the purpose of qualitative analysis only such reactions are applicable as are easily perceptible to our senses. A reaction is known to take place: (*a*) by the formation of a precipitate; (*b*) by a change of color; (*c*) by the evolution of a gas. In other words, the sense of sight is used chiefly in qualitative analysis, and most of the reactions employed are visual ones. The sense of smell also aids in identifying many substances. Thus the vapors of hydrogen sulfide, hydrogen cyanide, bromine, carbon disulfide, and a great many other substances have very characteristic odors. Some of these vapors are poisonous, so that in trying the odor

it is best to waft a little of the vapor, by a motion of the hand over the substance to be tested, in such a way that the vapor reaches the nostrils greatly diluted with air. The sense of taste is sometimes useful, but is rarely employed on account of the danger of poisonous effects. The sense of touch sometimes furnishes a little aid; thus graphite has a peculiar, greasy feeling, and paralysis of the tongue or eyelid is temporarily imparted by the alkaloid cocaine and certain allied substances.

As a rule, the characteristic reactions of qualitative analysis take place by adding a solution containing a substance called *the reagent* to a solution obtained from a solution of the substance which is being analyzed. These reactions are called reactions *in the wet way* to distinguish them from tests that are made *in the dry way* by fusing the sample with a flux such as sodium carbonate, sodium metaphosphate, or borax, or by heating the sample in the flame on a platinum wire or on charcoal.

The *law of mass action* is one of the most important generalizations in connection with the study of analytical chemistry. From the study of reactions that take place slowly and do not go to completion, Guldberg and Waage in 1867 showed that *the rate at which a chemical reaction takes place is proportional to the active masses of the reacting substances.* If two substances A and B react to form two other substances C and D in the sense of the equation

$$A + B \rightleftarrows C + D$$

the reaction will stop when the rate at which C and D react to form A and B is exactly equal to the rate at which A and B react to form C and D. If we express the *active masses* of these four substances by the symbols $[A]$, $[B]$, $[C]$, and $[D]$ the reaction comes to a state of equilibrium when

$$\frac{[C] \times [D]}{[A] \times [B]} = k$$

The value k is called the equilibrium constant, or is sometimes given special names such as *ionization constant, hydrolysis constant,* etc. If, instead of a simple reaction involving one molecule of each reacting substance, the reaction takes the form

$$mA + nB + \ldots \rightleftarrows pC + qD + \ldots$$

then the state of equilibrium is expressed mathematically as follows:

$$\frac{[C]^p \times [D]^q}{[A]^m \times [B]^n} = k$$

In these mass-action equations the values $[A]$, $[B]$, $[C]$, etc., refer to concentrations, or quantities present in a unit volume. It is customary

to express the concentrations in *moles per liter*. One mole of any substance is its molecular weight in grams.

The mass-action law applies to a state of *homogeneous equilibrium*. A homogeneous system is one in which every part of it is like every other part. A mixture of two solid substances is not homogeneous. A solution, on the other hand, is homogeneous when it is thoroughly mixed, since it is impossible to distinguish any difference between different portions of the solution. Similarly a mixture of gases represents a homogeneous system. Such homogeneous systems are called *phases*. A mixture of a solid, a solution, and a gas represents three phases; two solids, two phases; two immiscible liquids, two phases.

This law of mass action embodies one of the most important principles utilized in analytical chemistry. It enables one to understand why most reactions take place and to establish conditions under which these reactions will occur to the best advantage. The law has been verified by a great many quantitative as well as qualitative experiments. It has been studied, for example, in connection with the formation and decomposition of phosphorus pentachloride.

When chlorine gas reacts with cold phosphorus trichloride, the solid pentachloride is formed; but if this substance is heated, it breaks down into its constituents. The reaction is reversible and may be expressed as follows:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

At any given temperature an equilibrium exists which can be expressed mathematically, according to the mass-action law,

$$\frac{[PCl_3] \times [Cl_2]}{[PCl_5]} = k$$

in which $[PCl_3]$, $[Cl_2]$ and $[PCl_5]$ represent the concentrations at the time when equilibrium has been reached.

If we desire to volatilize phosphorus pentachloride so that the least possible dissociation will take place, the above equation shows us how this may be brought about.

If either $[PCl_3]$ or $[Cl_2]$ be increased, then in order that the value of the fraction

$$\frac{[PCl_3] \times [Cl_2]}{[PCl_5]}$$

shall remain constant, it is evident that the concentration $[PCl_5]$ must become greater; or, in other words, the dissociation of the pentachloride becomes less and there will be practically no dissociation if the pentachloride is volatilized in an atmosphere of phosphorus trichloride or of

chlorine. In this way, Wurtz obtained for the density of phosphorus pentachloride 6.80–7.42, instead of the calculated value 7.2.

At Stassfurt the mineral carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) occurs, which was evidently formed by precipitation from solutions containing the chlorides of magnesium and potassium. This double salt is less soluble than pure magnesium chloride and more soluble than pure potassium chloride. If carnallite is dissolved in water and the solution allowed to evaporate until crystals are deposited, it will be found that the crystals consist of potassium chloride. When the carnallite dissolves in water, the double salt is decomposed, more or less completely according to the dilution,

$$MgCl_2 \cdot KCl \rightleftarrows MgCl_2 + KCl$$

and for every concentration the equation holds:

$$\frac{[MgCl_2] \times [KCl]}{[MgCl_2 \cdot KCl]} = \text{a constant}$$

If we wish to recrystallize the carnallite, the breaking down of the double salt must be prevented as much as possible, and to do this it is merely necessary to add an excess of $MgCl_2$. As a matter of fact, the mineral is recrystallized at Stassfurt from a 23 per cent solution of magnesium chloride.

This law of mass action applies to all reactions involving chemical equilibria that take place in a homogeneous phase; *i.e.*, it can be applied to all reactions which take place between gases and to all those that take place in solution. The law shows that when the concentration of any substance participating in a chemical reaction is increased, this increases the tendency for the reaction to take place in the direction by which this substance is decomposed; when any substance formed by means of a chemical reaction is removed, this increases the tendency for the reaction to proceed in the direction by which this substance is formed. The formation of a precipitate or the escape of a gas, as fast as the substance is formed by means of a chemical reaction, tends to make the reaction take place more completely. If the gas is all boiled off, the reaction by which it is formed will take place completely. Similarly, if any precipitate were absolutely insoluble in water, the reactions by which this substance is formed would take place completely.

Theory of Electrolytic Dissociation or Ionization

The theory of ionization was proposed in 1887 by the Swedish chemist, Svante Arrhenius, to account for irregularities in the behavior of aqueous solutions as compared with non-aqueous solutions. It had been found possible to determine the approximate molecular weight of a substance

by measuring the lowering of the freezing point or the raising of the boiling point caused by dissolving a definite quantity of the substance in a known quantity of a suitable non-aqueous solvent. As a rule, the change in the freezing point or boiling point of a given solvent is the same when a mole of any substance is dissolved in 1000 g of solvent. The same is true of aqueous solutions if the substance dissolved is a *non-electrolyte* or, in other words, if the aqueous solution does not conduct electricity much better than water itself does. When the freezing point or boiling point of a solution of an electrolyte is measured and an attempt is made to estimate the molecular weight of the dissolved substance, the value obtained is much too low; the solution acts as if more molecules of dissolved substance were present than we have reason to believe from other data.

Other physical properties of the aqueous solutions of electrolytes, such as the vapor pressure and the osmotic pressure, point to the same conclusion.

Michael Faraday in his study of the laws governing electrolysis, the results of which were published in 1834, assumed that the first action of the electric current during electrolysis was to split the original molecules into smaller particles which he called *ions*.* According to Arrhenius, the splitting of the molecule into ions takes place without the aid of the electric current: the ions are present in aqueous solutions as soon as the substance is dissolved.

Although historically the theory of ionization was developed from the study of the purely physical properties of aqueous solutions such as the freezing point, boiling point, vapor pressure, osmotic pressure, and behavior toward an electric current, the theory is of special importance in explaining the chemical behavior of these solutions.

When an aqueous solution of barium chloride is mixed with dilute sulfuric acid, a white crystalline precipitate of barium sulfate forms. A precipitate of identically the same chemical composition can be formed from any soluble barium salt by using a solution of any soluble sulfate instead of sulfuric acid.

The addition of silver nitrate to an aqueous solution of barium chloride causes the formation of a white, curdy precipitate of silver chloride which darkens on exposure to light. The same precipitate is formed when hydrochloric acid or any other chloride is used instead of the barium chloride and when any other soluble silver salt is used instead of silver nitrate.

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* This and other terms used by Faraday in 1834 were suggested by William Whewell, an eminent scholar and teacher (1794–1866).

Similarly, aqueous solutions of all acids show certain properties. Blue litmus is turned red, carbonates are decomposed with effervescence, and metals are dissolved. These so-called *acid properties* are due to the hydrogen of acids, which behaves in an essentially different manner from the hydrogen of other compounds.

Bases also show certain characteristic reactions which can be traced to the hydroxide, OH, that they contain. An aqueous solution of a base turns red litmus blue and reacts with the hydrogen of an acid to form water.

E. C. Franklin, *J. Am. Chem. Soc.* **46,** 2137 (1924), in studying the properties shown by solutions of various substances in anhydrous liquid ammonia, has proposed to broaden the definition of acid, base, and salt and has pointed out that NH_4^+ formed by $NH_3 + H^+$ can be considered to be an acid in such a solution, and that the formation of NH_4^+ in the NH_3 solution can be compared to the formation of H_3O^+ by the hydration of the hydrogen ion in an aqueous solution: $H^+ + H_2O \rightarrow H_3O^+$.

N. F. Hall, *The Nucleus,* **6,** 91 (1929); *J. Chem. Education,* **7,** 782-93 (1930), has accepted similar ideas with respect to solutions in anhydrous acetic acid and like solvents. Brönsted, *Rec. trav. chim.,* **42,** 718-28 (1923); *J. Phys. Chem.,* **30,** 777 (1926); *Ber.,* **61,** 2049 (1928), Lucas, *Chemistry & Industry,* **42,** 43 (1923), and Bjerrum, *Chem. Rev.,* **16,** 287 (1935), have also attempted to broaden the concept of acid, base, and salt along similar lines, and, perhaps unfortunately, these ideas have been adopted by various writers of recent textbooks as " the modern definitions of acid, base, and salt," although these definitions have been adopted, with respect to aqueous solutions, only by a very small minority of chemists.

In this so-called " modern " conception, an acid is defined as a *donor* of hydrogen ions and a base is a *receiver* of hydrogen ions. Great stress is laid upon the fact that the hydrogen ion is hydrated in aqueous solution so that, according to this view, the hydrogen ion is as evanescent as *nascent* hydrogen and is capable of only momentary existence. The product, H_3O^+, of the reaction of hydrogen ion (or proton) and water is called the *hydronium* ion by some and the *oxonium* ion by others.

No further attention will be paid to these ideas in this book because: (1) they are not necessary or helpful in the understanding of the reactions that take place in aqueous solutions; (2) the nomenclature is confusing, because most of the literature of today, and all that of the last fifty years, has been written from another point of view; (3) the insistence on the fact that what we have for fifty years been calling the hydrogen ion, H^+, is really a hydrated ion, H_3O^+, is superfluous, for we have been aware of this fact during most of these years, just as we know that the hydroxide ion, OH^-, is probably $H_3O_2^-$ or $H_5O_3^-$. There is even stronger evidence that cupric, nickelous, cobaltous, etc., ions are hydrated, and there is just as much reason to say that Cu^{++} is not likely to exist in aqueous solution as to insist that H^+ is really H_3O^+.

The aqueous solutions of acids, bases, and salts, therefore, show reactions which are characteristic not so much of the dissolved substance as a whole as of its constituents. This is a very important point. It enables us to test for the constituents of a solution more or less independently of the other constituents which may be present. We can test for barium in just the same way whether it is present as chloride or as

nitrate, and we can test for chlorine by the same reagent no matter whether the chlorine was originally present as hydrochloric acid or as some other chloride. This is remarkable, because the chemical properties of a compound are usually quite different from the sum of the properties of its constituents. The properties of the chemical compound water show little similarity to the properties of either hydrogen or oxygen gas. The properties of sodium iodide are altogether different from those of metallic sodium and of free iodine, and those of potassium chlorate are quite distinct from the properties of the potassium, chlorine, and oxygen which it contains. Aqueous solutions of acids, bases, and salts, however, actually do show additive properties, *i.e.*, sodium chloride in solution shows properties which the sodium of any other sodium salt will show, plus other properties which any other chloride will show. This suggests the hypothesis that the aqueous solution of an acid must contain its hydrogen, to some extent at least, in the same condition as the aqueous solution of any other acid; that an aqueous solution of a base must contain a part, at least, of its hydroxide in the same condition as the aqueous solutions of any other base; and that the metals and non-metals of salts must be present in very much the same condition irrespective of the nature of the original salt.

Aqueous solutions of the acids, bases, and salts referred to in the above discussion all conduct electricity very much better than pure water does. They are electrolytes. According to the theory of electrolytic dissociation, or ionization, all electrolytes in aqueous solution exist, at least to some extent, as electrically charged atoms or atom groups called *ions*.

When sodium chloride is dissolved in water, it breaks up, according to the equation

$$NaCl \rightleftarrows Na^+ + Cl^-$$

into positively charged sodium ions and negatively charged chloride ions.

Nearly all salts, acids, and bases behave like common salt. Thus sodium sulfate decomposes according to the equation

$$Na_2SO_4 \rightleftarrows Na^+ + Na^+ + SO_4^{--}$$

and sodium hydroxide $NaOH \rightleftarrows Na^+ + OH^-$.

By this theory of electrolytic dissociation the phenomena of electrolysis may be explained very simply: If we insert the two poles of a source of electricity into an electrolyte, one of the poles, the anode, is charged with positive electricity, and the other, the cathode, with negative electricity. The electropositive anode repels the electropositive ions (cations) and attracts the electronegative ions (anions);

and the latter, as soon as they come in contact with the anode, give up their negative electricity, become neutral, and separate out.* The same thing happens at the cathode, where the electropositive ions are discharged.

The reason why an aqueous solution of any barium salt reacts with any soluble sulfate to form barium sulfate is that barium ions cannot exist in the presence of sulfate ions to any appreciable extent without forming barium sulfate, and the reaction is expressed best as follows:

$$Ba^{++} + SO_4^{--} \rightleftarrows BaSO_4$$

Similarly, the reaction between barium chloride and silver nitrate is merely that of silver ions and chloride ions uniting to form silver chloride,

$$Ag^{+} + Cl^{-} \rightleftarrows AgCl$$

Almost all the reactions of qualitative analysis that take place in aqueous solutions are reactions in which ions react with ions rather than molecules with molecules.

Take, for example, the action of a dilute solution of an acid upon a dilute solution of a base. The reaction that takes place is merely the uniting of hydrogen ions with hydroxide ions to form undissociated water. This is known to be true, because if the reaction takes place with 1 g of hydrogen and 17 g of hydroxide ions, the heat evolved is 13,700 calories. This same amount of heat is evolved when an equivalent amount of a dilute solution of hydrochloric acid is neutralized by a dilute solution of potassium hydroxide, or when the hydrochloric acid is replaced by another acid such as nitric acid; it represents merely the heat of formation of a molecular weight in grams (one *mole*) of water from hydrogen ions and hydroxide ions.

Similarly it can be shown that when an acid acts on a metal with the liberation of hydrogen gas, the quantity of heat which is developed depends only on the nature of the metal and is independent of the acid. The anion of the acid really does not take part in the reaction at all.

The main assumptions of the Arrhenius theory of electrolytic dissociation are as follows: When an acid, a base, or a salt dissolves in water, its molecules are usually dissociated immediately into smaller

* The ion that carries the current from one electrode to the other is not always discharged at its destination. Sometimes it reacts with the electrode, which dissolves, and sometimes it is easier to set free hydrogen and oxygen from water than it is to discharge the ion that carried the current. Thus, in the electrolysis of sodium chloride solution, no sodium is formed at the cathode, except when the cathode consists of mercury, because it is easier to set free hydrogen from water than to discharge sodium ions. If any free sodium were formed it would react at once with water.

fragments called ions. These ions are charged with electricity. The sum of the positive charges residing on the cations is exactly equal to the sum of the negative charges residing upon the anions, and the whole solution is electrically neutral. The dissociation is a reversible reaction, and all electrolytes may be considered to be completely ionized at infinite dilution. Except for the dependence resulting from the electrical charges and the consequent attractions and repulsions between ions, the ions may be regarded as independent constituents with individual and specific chemical and physical properties. If a substance dissolves in water and is only partly dissociated, then when the ions are removed, either by electrolysis or as a result of chemical reaction, the substance will at once continue to form ions.

Though it is true that most inorganic acids, bases, and salts are *ionogens*,* yet the extent to which ionization takes place when the substance is dissolved in water varies greatly. Thus a molecular weight in grams of hydrogen chloride dissolved in 10 l of water yields about seventy times as many hydrogen ions as an equivalent quantity of acetic acid; a similar comparison can be made with regard to sodium hydroxide solution and ammonium hydroxide. Since the *strength* of an acid is determined by the concentration of active hydrogen ions, hydrochloric acid is about seventy times as strong an acid as acetic acid and sodium hydroxide or potassium hydroxide is nearly seventy times as strong a base as ammonium hydroxide.

On the other hand, a molecular weight of acetic acid will neutralize the same weight of sodium hydroxide that a molecular weight of hydrochloric acid does, and a molecular weight of ammonium hydroxide will neutralize the same weight of acid that a molecular weight of sodium hydroxide does. In a solution of sodium hydroxide and of hydrochloric acid of the above concentration the original molecules are considered entirely ionized, and when the acid and base are mixed the principal change is the union of hydrogen ions and hydroxyl ions to form water. When acetic acid of the same concentration is used, there is present at the start only 1.3 per cent of all the hydrogen in the form of ions. These ions will at once react with hydroxide ions to form water, but there is always a tendency for the acetic acid to ionize, and when the ions disappear as fast as they are formed the ionization continues until all the molecules of acetic acid have dissociated. In the

* An *ionogen*, as its name indicates, is a substance capable of forming ions; according to the valence theory of G. N. Lewis, *J. Am. Chem. Soc.*, **36**, 762 (1916); cf. Langmuir, *ibid.*, **41**, 868, 1543 (1919), an ionogen is a *polar* compound in which the valence electron has passed from one atom to another forming, when only two atoms are involved, an electric dipole.

neutralization of acetic acid with sodium hydroxide, the final heat effect will not be simply that of the union of hydrogen ions with hydroxide ions, but will also involve the energy required to cause the acetic acid to ionize. When a substance ionizes as soon as it dissolves, the heat effect of ionization cannot easily be distinguished from the heat of solution. Just as some substances dissolve with absorption of heat and some with evolution of heat, so it is found that the ionization process may likewise be associated with either an absorption or evolution of heat.

It is interesting to note, and this is a matter of considerable importance, that the salts of weak acids and of weak bases are usually ionized nearly as much as the salts of strong acids or of strong bases.

When a dibasic acid dissolves in water, the two hydrogen atoms do not ionize to an equal extent. The ionization takes place in two stages. Thus with sulfuric acid the first stage takes place in the sense of the equation:

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^-$$

The fact that the reaction does not necessarily take place completely is indicated by using the double arrow sign instead of the equality sign. When the above reaction stops there is a state of equilibrium between the three substances H_2SO_4, H^+, and HSO_4^-. The HSO_4^- undergoes a secondary ionization as follows:

$$HSO_4^- \rightleftarrows H^+ + SO_4^{--}$$

The extent to which these reactions take place depends upon the dilution. If half a molecular weight in grams of sulfuric acid is dissolved in 10 l of water, the primary ionization will take place to about 90 per cent of the entire quantity of acid present and the secondary ionization to less than 50 per cent. If the solution is extremely dilute, both reactions will take place almost completely.

In carbonic acid, the primary stage

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

ordinarily takes place only to a fraction of 1 per cent and the secondary stage

$$HCO_3^- \rightleftarrows H^+ + CO_3^{--}$$

to an inappreciable extent (cf. p. 11). With hydrogen sulfide the relations are similar.

On the other hand, the salts of these weak acids will ionize completely as follows:

$$Na_2CO_3 \rightleftarrows Na^+ + Na^+ + CO_3^{--}$$

$$Na_2S \rightleftarrows Na^+ + Na^+ + S^{--}$$

The following table will be found useful in studying the ionization of electrolytes. It gives the approximate percentage of active hydrogen ions present in 0.1 *N* solution at 25°. In the case of the strong electrolytes (*i.e.*, those which are ionized to about 50 per cent or more) the values represent the actual concentration of hydrogen ions multiplied by the activity coefficient (see p. 12). In the case of the weak electrolytes it is not necessary to take the activity factor (see p. 13) into consideration. In the case of polybasic acids, the value opposite the formula of the acid shows the fraction of the whole molecule which undergoes the primary ionization into one hydrogen ion, that opposite an ion with a univalent charge shows the extent to which this ion undergoes a secondary ionization, and that opposite an ion with a bivalent charge shows the extent to which it undergoes a tertiary decomposition, forming a third hydrogen ion from the original neutral molecule of the acid.

Apparent Ionization Values of Common Electrolytes

In 0.1 *N* Solution	Per Cent
Salts of the type B^+A^- (e.g., KNO_3)	84
Salts of the type $B_2^+A^{--}$ or $B^{++}A_2^-$ (e.g., K_2SO_4 or $BaCl_2$)*	73
Salts of the type $B_3^+A^{---}$, or $B^{+++}A_3^-$ (e.g., $K_3[Fe(CN)_6]$ or $AlCl_3$)	65
Salts of the type $B^{++}A^{--}$ (e.g., $MgSO_4$)	40
KOH, NaOH*	90
$Ba(OH)_2$*	80
NH_4OH	1.3
HCl, HBr, HI, HSCN, HNO_3, $HClO_4$, H_2SO_4, H_2CrO_4	90
H_3PO_4, H_3AsO_4, H_2SO_3, $H_2C_2O_4$, HSO_4^-	20–45
HNO_2, HF	7–9
$HC_2H_3O_2$, $HC_2O_4^-$, HSO_3^-	1–2
H_2S, H_2CO_3, $H_2PO_4^-$, $HCrO_4^-$	0.1–0.2
HBO_2, $HAsO_2$, HCN, HCO_3^-, HClO	0.002–0.008
HS^-, HPO_4^{--}, $HAsO_4^{--}$	0.0001–0.0002
HOH (at 25°)	0.000,000,1

The activity coefficients of strong electrolytes varies at different concentrations and is influenced greatly by the presence of other ions. Thus an aqueous solution of hydrogen chloride in the presence of considerable alkali chloride shows a greater concentration of active hydrogen than does one of hydrogen chloride in pure water (cf. p. 13). Acetic acid is a stronger acid in the presence of considerable sodium chloride (cf. p. 27), which is interesting because the effect of adding sodium acetate to a solution containing hydrogen ions is to lessen the concentration of hydrogen ions as a result of forming undissociated acetic acid (see p. 49).

* Exceptions: $CdCl_2$ ionizes to about 47 per cent; $HgCl_2$, to about 0.01 per cent; and $HgBr_2$, HgI_2, and $Hg(CN)_2$, less than $HgCl_2$.

Nomenclature of the Ions

As already mentioned (p. 5), Faraday in 1834 was the first to use the words *ion, cathode, cation, electrode, anode,* etc. All these names are derived from Greek roots. Faraday's idea was that the electricity entered the solution at the positive pole and passed *down* to the negative pole. The word *ion* is the Greek word (spelled in Latin letters) for *wanderer* or *traveler.* Anode is from the Greek ἀνά (ana), up, and ὁδός (odos), a path. Cathode is from the Greek κατά (kata), down, and ὁδός. The two electrodes are considered as the doors or paths by which the current enters and passes out of the solution.

Two methods are in common use for designating the ions. Thus the ions of hydrochloric acid are designated as H^+ and Cl^- or as $H^{\cdot}$ and Cl'. Small plus and minus signs are used in this book rather than the dots and dashes simply because this is the present practice in the journals published by the American Chemical Society. Many writers prefer to use the other system because it takes up less room; with the polyvalent ions the use of the plus and minus signs is often very cumbersome.

The Mass-Action Law in Terms of Activities

Qualitative analysis is, for the most part, concerned with the chemistry of dilute solutions, and the majority of the reactions are based upon solubility relations. In the study of these relations, the mass-action law plays an important part.

In the ordinary course of an analysis it is very common to deal with solutions which are supersaturated with this or that substance of very low solubility, and, for that reason, the chemist is often content to use approximations in his computations. In most of the applications of the mass-action law, therefore, it is sufficiently accurate to assume that the *concentrations* (always expressed in moles per liter) of the reacting substances are equal to the *active masses.* This is true of perfect gases at low partial pressures and of dilute solutions of non-electrolytes. An appreciable error is introduced, however, in computations involving compressed gases or solutions of strong electrolytes. The following relation holds between the activity, a (or the active mass) and its concentration c (always expressed in moles per liter)

$$a = cf$$

The value f is called the *activity coefficient.*

The equilibrium of the reaction

$$A + B \rightleftarrows C + D$$

is, therefore,

$$\frac{[C][D]f_C \cdot f_D}{[A][B]f_A \cdot f_B} = k$$

where the letters in brackets denote the concentrations of A, B, C, and D in moles per liter and f_A, f_B, etc., are the corresponding activity coefficients.

These activity coefficients do not have constant values, but, as indicated above, under any given conditions, the activity is proportional to the concentration. The activity coefficient of an ion is affected by the presence of other ions in solution. In infinitely dilute solutions f approaches unity and then the activity, a, becomes equal to the concentration, c. With increasing concentration of the ion, the value of f decreases and eventually reaches a minimum. The activity coefficient of an ion in a solution of an electrolyte depends upon the valence of the ion, the properties of the ion, and the concentrations and kinds of other ions present.

Our knowledge of the activity coefficients under varying conditions is meager. Some idea of the way they vary in different concentrations of aqueous solutions is given by the following table:*

MEAN ACTIVITY COEFFICIENTS OF CERTAIN IONS

Molar Concentration	0.005	0.01	0.02	0.05	0.10	0.20	0.50	1.00	3.00
Limiting Law for A^+B^-	0.921	0.890	0.848	0.771	0.692	0.595	0.439	0.313	0.133
Theory for A^+B^-	0.926	0.900	0.866	0.809	0.756	0.698	0.618	0.559	0.478
HCl	0.829	0.904	0.874	0.830	0.795	0.766	0.757	0.810	1.320
NaCl	0.928	0.904	0.876	0.829	0.789	0.742	0.683	0.659	0.709
KCl	0.926	0.899	0.866	0.812	0.763	0.713	0.649	0.601	0.571
KOH	0.927	0.901	0.868	0.810	0.759	0.710	0.671	0.679	0.903
KNO_3	0.829	0.899	0.863	0.794	0.724	0.653	0.543	0.449	.....
$AgNO_3$	0.925	0.896	0.858	0.787	0.717	0.633	0.501	0.390	.....
KIO_3, $NaIO_3$	0.924	0.895	0.856	0.784	0.714	.....	.....	.....	.....
Theory for $A^{++}B^{--}$	0.562	0.460	0.359	0.238	0.165	0.101	0.066	0.045	.....
$MgSO_4$	0.572	0.471	0.378	0.262	0.195	0.142	0.091	0.067	.....
$CuSO_4$	0.560	0.444	0.343	0.230	0.164	0.018	0.066	0.044	.....
Theory, $A^{++}B_2^-$ or $A_2^+B^{--}$	0.776	0.710	0.634	0.523	0.439	0.362	0.274	0.229	.....
$BaCl_2$	0.781	0.725	0.659	0.556	0.496	0.440	0.396	0.399	.....
$Pb(NO_3)_2$	0.763	0.687	0.596	0.464	0.373	0.275	0.168	0.112	.....
K_2SO_4	0.781	0.715	0.642	0.529	0.441	0.361	0.262	0.210	.....

* These values were furnished by Professor M. S. Sherrill, of the Massachusetts Institute of Technology.

Equilibrium Between a Solid and Two Liquids

Although water, either pure or containing dissolved acid, is the solvent most used in analytical chemistry, it often happens that a substance is more soluble in some other liquid. Thus free iodine is about 400 times as soluble in carbon disulfide as it is in water. When iodine is in contact with both carbon disulfide and water, which are only slightly soluble in one another, it will dissolve chiefly in the carbon disulfide. Moreover, if an aqueous solution of iodine is shaken with carbon disulfide, the latter, when it separates out beneath the water, will contain nearly all the iodine. A state of equilibrium then exists between the solution of iodine in water and the solution of iodine in carbon disulfide. Such an equilibrium is governed by the so-called *distribution law* or *law of partition.* If C_A represents the concentration of a substance in a solvent A and C_B is its concentration in a solvent B, equilibrium is reached at a given temperature when

$$\frac{C_A}{C_B} = k$$

This is the mathematical expression of the distribution law. The constant, k, is called the *distribution coefficient.* In this simple form, it is important to note that the law holds only when each concentration is expressed in terms of the same molecular species. Thus if a substance is dissociated to a large extent in one solvent and scarcely at all in another, the concentrations involved must be those of the undissociated salt in each case. It is quite common to find that the *ions* of a substance are much more soluble in water than in any other solvent whereas for the undissociated substance the relations are reversed. Iodine dissolves to a greater extent in a solution of potassium iodide than it does in pure water, owing to the formation of I_3^-. In such a solution the following equilibrium exists:

$$I^- + I_2 \rightleftarrows I_3^-$$

If such a solution is shaken with carbon disulfide, the distribution law holds only for the free iodine held in solution as such in each liquid.

For iodine in pure water and iodine in carbon disulfide, the distribution coefficient is $\frac{1}{400}$ at room temperature. Theoretically it is impossible to remove all the iodine from water by shaking with carbon disulfide, but if the carbon disulfide is removed, with the aid of a separatory funnel, and the aqueous solution is shaken with fresh carbon disulfide, it is evident that the quantity of iodine remaining with the water is negligible, or can be made so by repeating the operation.

Sometimes in testing for the halides it is desirable to remove free halogen from the aqueous solution; to accomplish this, the distribution prin-

ciple is utilized. Ferric chloride is much more soluble in ether and hydrochloric acid than it is in water and hydrochloric acid; to detect the minor constituents of iron or steel, a large sample of the original material is taken and the ferric chloride removed by shaking the hydrochloric acid solution with ether. Perchromic acid is more soluble in ether than in water; by shaking the dilute aqueous solution with a little ether, a concentrated solution in the ether is obtained and the presence of the chromium shown by the beautiful blue color.

Influence of Changes in Concentration upon the Ionization of Electrolytes

If we assume 1 mole of a weak electrolyte, such as a solution of NH_3 in v l of water, the original substance will be partly ionized according to the equation

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

into ammonium and hydroxide ions. If α is the fraction of the base ionized in the sense of the above equation, then the non-ionized part will amount to $1 - \alpha$.

Since the total quantity of water present does not change appreciably, we can neglect it in the mass-action expression, and when equilibrium is reached the concentrations per liter are

$$H_2O + NH_3 \rightleftarrows NH_4^+ + OH^-$$

$$\frac{1-\alpha}{v} \qquad \frac{\alpha}{v} \qquad \frac{\alpha}{v}$$

and according to the *mass-action* law

$$k \cdot \frac{1-\alpha}{v} = \frac{\alpha^2}{v^2}$$

$$k = \frac{\alpha^2}{(1-\alpha)v}$$

This is called *Ostwald's dilution law.* It shows that, if we start with a given quantity of a weak acid or of a weak base, the actual quantity of H^+ from the acid or of OH^- from the base will increase steadily as we dilute the solution of the acid or base, although the actual concentration will diminish. Thus if 1 mole of acetic acid is dissolved in 1 l of water, the concentration of H^+ at room temperature is 0.004 molal and the acid is 0.4 per cent ionized. If the same quantity of acetic acid is dissolved in 1500 l of water, the concentration of the H^+ from the acetic acid is about 0.000097 mole but the ionization is now 14.7 per cent of the total quantity of acetic acid present.

Another way of expressing the application of the mass-action law to the ionization of a weak electrolyte is the following:

Let [HA], [H^+], and [A^-] represent the respective concentrations of a weak acid, HA, which ionizes to some extent into H^+ and A^- ions. Then

$$HA \rightleftarrows H^+ + A^-$$

When equilibrium is reached, the mass-action law reads:

$$\frac{[H^+][A^-]}{[HA]} = k_a$$

Unless the acid is very weak, we can disregard the hydrogen ions from water and assume that [H^+] and [A^-] are equal. Moreover, if the acid is less than 10 per cent ionized and we are satisfied with an accuracy of two significant figures, we can assume that the concentration of [HA] is approximately the total quantity of the acid that is present. Calling this value c, the above equation becomes

$$\frac{[H^+]^2}{c} = k_a \quad \text{and} \quad [H^+] = \sqrt{k_a c}$$

A corresponding expression holds for the OH^- concentration of the aqueous solution of a weak base:

$$[OH^-] = \sqrt{k_b c}$$

The following table gives the ionization constants of some weak acids and weak bases:

IONIZATION CONSTANTS OF WEAK ACIDS AT 25°

(In the case of dibasic acids, K_1 signifies the ionization constant for the first replaceable H atom and K_2 is the ionization constant for the second H atom.)

Name	K_a	Name	K_a
Acetic acid	1.7×10^{-5}	Oxalic acid K_1	6.5×10^{-2}
Arsenic acid, K_1	5.0×10^{-3}	Oxalic acid K_2	6.1×10^{-5}
Arsenious acid, K_1	6.0×10^{-10}	Phosphoric acid K_1	1.4×10^{-1}
Benzoic acid	6.7×10^{-5}	Phosphoric acid K_2	2.0×10^{-7}
Carbonic acid K_1	3.5×10^{-7}	Phosphoric acid K_3	3.6×10^{-13}
Carbonic acid K_2	5.0×10^{-11}	Tartaric acid K_1	9.6×10^{-4}
Citric acid K_1	8.7×10^{-4}	Tartaric acid K_2	2.9×10^{-5}
Citric acid K_2	1.8×10^{-5}	Pyrophosphoric acid K_1	1.4×10^{-1}
Citric acid K_3	4.0×10^{-6}	Pyrophosphoric acid K_2	1.1×10^{-2}
Formic acid	2.0×10^{-4}	Pyrophosphoric acid K_3	2.9×10^{-7}
Hydrogen sulfide K_1	5.7×10^{-8}	Pyrophosphoric acid K_4	3.6×10^{-9}
Hydrogen sulfide K_2	1.2×10^{-15}	Sulfuric acid, K_2	3.0×10^{-2}
Hydrocyanic acid	7.0×10^{-10}	Sulfurous acid K_1	1.7×10^{-2}
Nitrous acid	4.0×10^{-4}	Sulfurous acid K_2	1.0×10^{-7}

IONIZATION CONSTANTS OF WEAK BASES AT 25°

Name	Kb	Name	Kb
Ammonia	1.75×10^{-5}	Lead hydroxide	9.6×10^{-4}
Aniline	$4. \times 10^{-10}$	Methylamine	4.4×10^{-4}
Hydrazine	$3. \times 10^{-6}$	Pyridine	1.4×10^{-9}

Strong electrolytes, whether acids, bases, or salts, do not have ionization constants. In other words, the value K is not constant for different concentrations. If the ionization is 100 per cent, the value of K would be infinity, which is certainly not a useful value. The value 1 has sometimes been assumed for the ionization constant of a strong acid or base, and this is a large value compared with the constants given in the above tables. In approximate computations it is best to assume that strong electrolytes are completely ionized or use the approximations given on page 11. See also page 13.

Ionization of Water. The Hydrogen Exponent, p_H

The ionization of water

$$H_2O \rightleftarrows H^+ + OH^-$$

takes place to a very slight extent and water itself is a very weak electrolyte. According to the mass-action law, the equilibrium between H^+, OH^-, and H_2O is expressed by the equation

$$\frac{[H^+][OH^-]}{[H_2O]} = k$$

but since the concentration of the water (in moles per liter) is not changed appreciably by its ionization and $[H_2O]$ is very large in comparison with $[H^+]$ and $[OH^-]$, it is best to consider the concentration of the undissociated water a constant and we then have

$$[H^+][OH^-] = k_w$$

The value of k_w, called the *ion product* (or *ionization product*) of water, is constant at any given temperature but increases slowly with rise of temperature as the following table shows:

ION PRODUCT, k_w, OF WATER AT VARIOUS TEMPERATURES

$[H^+] \times [OH^-] = k_w$

Temp.	kw	Temp.	kw
0°	0.12×10^{-14}	60°	0.93×10^{-13}
10°	0.3×10^{-14}	70°	2.1×10^{-13}
18°	0.59×10^{-14}	80°	2.3×10^{-13}
25°	1.0×10^{-14}	90°	3.6×10^{-13}
30°	1.5×10^{-14}	100°	5.1×10^{-13}
50°	5.5×10^{-14}		

The constant k_w is of great importance in the study of analytical chemistry and has helped to clarify our knowledge concerning the neutralization of acids and bases. In pure water, and at room temperature, the concentration of both H^+ and OH^- is 10^{-7} mole per liter because the product is 10^{-14}. This does not by any means imply that any sample of distilled water in the laboratory is likely to have exactly this concentration of H^+ and OH^-. If the water has been exposed to the atmosphere, carbon dioxide will be absorbed and this is likely to make the concentration of H^+ about 20 times larger than 10^{-7} because water reacts with carbon dioxide to form carbonic acid. If, on the other hand, the water has been kept in a glass vessel it dissolves sufficient glass to become basic and, moreover, distilled water often contains a little dissolved ammonia arising from the nitrogenous matter present in the water that was distilled. Since the ion product, k_w, of water is a constant, for a given temperature, we can always tell what the OH^- concentration of an aqueous solution is if we know the H^+ concentration, and *vice versa*.

In potentiometric studies of H^+ concentration, it has been found that the so-called "single potential" of the hydrogen electrode is proportional to $\log \frac{1}{[H^+]}$, and this value is positive when the concentration of H^+ is less than 1. Because it is a positive number, it is a value which is easy to handle. For this reason, it has become common practice to express small concentrations of both H^+ and OH^- in terms of $\log \frac{1}{[H^+]}$ which is called the *hydrogen exponent*, or p_H.

To illustrate the relation between p_H and the concentration of H^+ or of OH^- it may be well to discuss a few typical examples. Since the logarithm of a fraction is the logarithm of the numerator minus the logarithm of the denominator and the logarithm of 1 is 0, it is clear that $\log \frac{1}{[H^+]}$ is obtained by subtracting the logarithm of H^+ from 0. This is sometimes expressed by saying that p_H is the *negative logarithm of the concentration of the hydrogen ion in moles per liter*. The term "negative logarithm" is another name for *cologarithm*, usually written *colog*.

If the hydrogen-ion concentration is 10^{-7}, the logarithm of 10^{-7} is -7 (usually written $\bar{7}$ and sometimes $3.00 - 10$), and the $p_H = 7$. This represents the true neutral point of water. The higher the p_H value, the lower is the concentration of hydrogen ion; solutions having a p_H less than 7 are more acid than water, and those having a p_H greater than 7 are more basic than water. When the $p_H = 6$ the solution contains 10 times as much H^+ as pure water does, and similarly $p_H = 5$ corresponds to a hydrogen-ion concentration 100 times that of pure water.

If the concentration of H^+ *is* 0.00046 *mole per liter, what is the* p_H *value?* In the conventional method of using logarithms the number is usually thought of as a number between 0 and 10 multiplied by a power of 10. The number 0.00046 can be written 4.6×10^{-4}. Then $\log \frac{1}{4.6 \times 10^{-4}} = \log \frac{10^4}{4.6}$, and to find the p_H we subtract the log of 4.6 from the log of 10^4, which is 4. Since the log of 4.6 = 0.66, the desired p_H is $4 - 0.66 = 3.34$.

Another way of arriving at the same result is this:

The log of 0.00046 is $\bar{4}.66$. In this case the minus sign is written above the 4 to show that it has a negative value whereas the mantissa in the logarithm is 0.66, a positive number, and represents the log of 4.6. The value $\bar{4}.66$ is really the same as -3.34, and $0.00046 = 10^{-3.34}$. Subtracting -3.34 from 0 (the log of 1) gives the value 3.34 as before.

What is the p_H of a solution which contains 0.00046 *mole of* OH^- *per liter?*

Just as it is convenient to express low concentrations of H^+ in terms of the "hydrogen exponent" or $\frac{1}{\log [H^+]}$, we can do the same with the concentration of OH^- and say that $p_{OH} = \frac{1}{[OH^-]}$, and similarly for the ion product of water we can say that $p_w = \log \frac{1}{Kw} = \log \frac{1}{10^{-14}} = 14$ at room temperature. Obviously

$$p_H + p_{OH} = p_w \quad \text{and} \quad p_H = 14 - p_{OH}$$

When $OH^- = 0.00046$, $p_{OH} = 3.34$ and $p_H = 14 - 3.34 = 10.66$.

The relation between p_H and p_{OH} is shown very clearly by the table* on p. 20 in which it is assumed that HCl and NaOH are completely ionized in the solutions mentioned.

Solubility Product

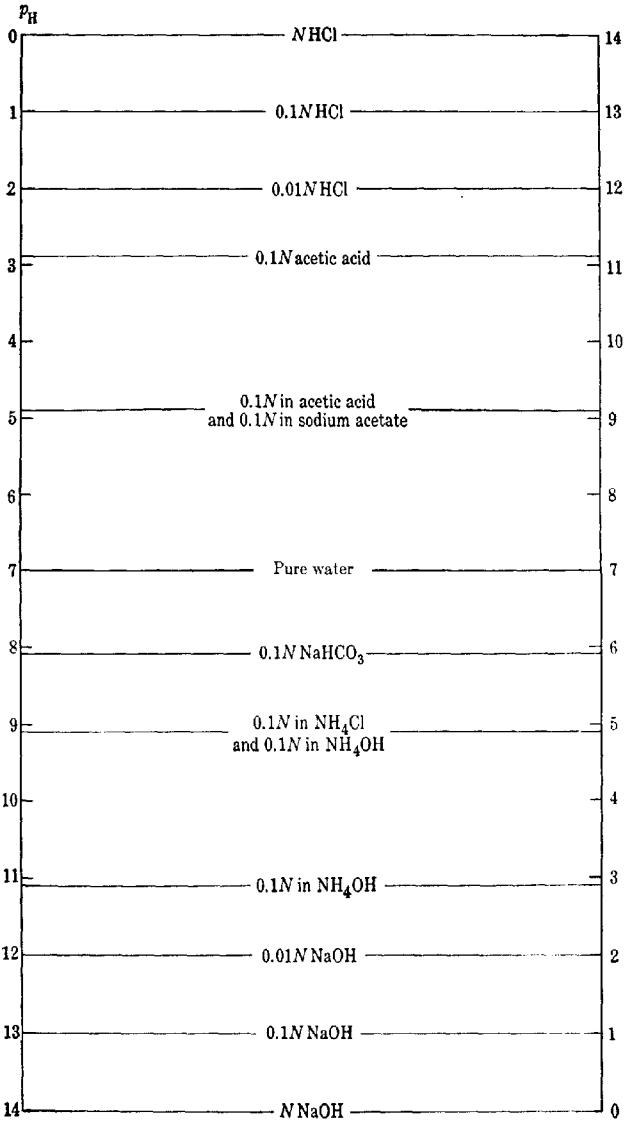
Silver chloride is slightly soluble in water; 0.00001 mole (1.5 mg) of the solid dissolves in 1 l of the solvent. When water is placed in contact with an excess of silver chloride, a state of equilibrium is soon reached between the solid and the solution. If more than this quantity of dissolved substance is present at any time, the solution is supersaturated and tends to precipitate silver chloride; if less, then more silver chloride will be dissolved. When equilibrium is reached the tendency of the salt to precipitate is equal to the tendency of the salt to dissolve.

The mass-action expression $\frac{[Ag^+]\,[Cl^-]}{[AgCl]} = k$ meets with difficulty here, because the concentration [AgCl] applies only to the non-ionized AgCl that is in solution and it is safe to assume that all the AgCl is ionized. It is customary to assume, in such cases, that the value $[Ag^+]\,[Cl^-]$ in a saturated solution of AgCl is a measure of the solubility of the AgCl at the temperature at which the solution was saturated. This "ion-concentration product," $[Ag^+]\,[Cl^-] = k_{AgCl}$, is called the *solubility product.*

If we are dealing with a substance such as PbI_2, the solubility product is $[Pb^{++}]\,[I^-]^2$, where $[Pb^{++}]$ and $[I^-]$ represent the concentrations, in moles per liter, of Pb^{++} and I^-, respectively, in water which is saturated with PbI_2. In general, if the substance A_mB_n ionizes into mA and nB ions, the solubility product, S_p, is found by the following equation:

$$S_p = [A]^m \times [B]^n = k\,[A_mB_n]$$

* Cf. Kolthoff and Sandell, *Textbook of Quantitative Analysis.*



p_H and p_{OH} scales at room temperature

in which k is the ionization constant and the concentrations are those of a *saturated solution.*

Experience has shown that the conditions are somewhat more complicated in concentrated solutions such as are obtained with the very soluble substances. In future discussion, therefore, the solubility will be expressed, as a rule, in terms of the solubility product only when the substance does not dissolve to a greater extent than 0.01 mole per liter. The table on page 13 shows that the "active masses" of binary salts of the type represented by AgCl correspond to an ionization of about 84 per cent in 0.1 N solution, and we have seen on page 15 that the ionization increases as the solution is diluted. In such a dilute solution as that of silver chloride (0.00001 N) the ionization is nearly 100 per cent. It is therefore logical, in such cases, to express the solubility in terms of the ions, whereas with very soluble substances it is better to measure the solubility in terms of the mass of dissolved substance.

In the following table the solubility of each substance is expressed in three ways: in grams of dissolved substance per liter, in moles per liter, and, finally, in terms of the solubility product, using moles per liter. The solubility of most of the substances given in the table is so slight that the quantity dissolved is negligible for most purposes. Whenever the word *insoluble* is used in this book it is with the understood limitation that no substance is absolutely insoluble in water.

SOLUBILITIES AND SOLUBILITY PRODUCTS AT ROOM TEMPERATURE

Substance	Solubility in Grams per Liter	Solubility in Moles per Liter	Solubility Product
$AgBr$	1.1×10^{-4}	5.9×10^{-7}	$[Ag] \times [Br] = 3.5 \times 10^{-13}$
$AgBrO_3$	1.7	7.1×10^{-3}	$[Ag] \times [BrO_3] = 5.0 \times 10^{-5}$
$Ag_2(CN)_2$	4.05×10^{-4}	1.5×10^{-6}	$[Ag] \times [Ag(CN)_2] = 2.2 \times 10^{-12}$
$AgCNS$	1.4×10^{-4}	8.5×10^{-7}	$[Ag] \times [CNS] = 7.1 \times 10^{-13}$
$AgCl$	1.5×10^{-3}	1.1×10^{-5}	$[Ag] \times [Cl] = 1.2 \times 10^{-10}$
Ag_2CO_3	3.0×10^{-2}	1.1×10^{-4}	$[Ag]^2 \times [CO_3] = 5.0 \times 10^{-12}$
$Ag_2C_2O_4$	3.5×10^{-2}	1.1×10^{-4}	$[Ag]^2 \times [C_2O_4] = 5.0 \times 10^{-12}$
Ag_2CrO_4	2.5×10^{-2}	7.5×10^{-5}	$[Ag]^2 \times [CrO_4] = 1.7 \times 10^{-12}$
$Ag_2Cr_2O_7$	8.3×10^{-2}	1.9×10^{-4}	$[Ag]^2 \times [Cr_2O_7] = 2.7 \times 10^{-11}$
AgI	3.0×10^{-6}	1.3×10^{-8}	$[Ag] \times [I] = 1.7 \times 10^{-16}$
$AgIO_3$	4.4×10^{-2}	1.5×10^{-4}	$[Ag] \times [IO_3] = 2.3 \times 10^{-8}$
Ag_2O	2.1×10^{-2}	9.0×10^{-5}	$[Ag] \times [OH] = 1.9 \times 10^{-8}$
$AgOH$	1.7×10^{-2}	1.4×10^{-4}	$[Ag] \times [OH] = 2.0 \times 10^{-8}$
Ag_3PO_4	6.5×10^{-3}	1.6×10^{-5}	$[Ag]^3 \times [PO_4] = 1.8 \times 10^{-18}$

SOLUBILITIES AND SOLUBILITY PRODUCTS AT ROOM TEMPERATURE — *Continued*

Substance	Solubility in Grams per Liter	Solubility in Moles per Liter	Solubility Product
Ag_2S	7.3×10^{-15}	3.4×10^{-17}	$[Ag]^2 \times [S] = 1.6 \times 10^{-49}$
Ag_2SO_4	8.0	2.6×10^{-2}	$[Ag]^2 \times [SO_4] = 7.0 \times 10^{-5}$
$BaCO_3$	8.1×10^{-3}	4.1×10^{-5}	$[Ba] \times [CO_3] = 7.0 \times 10^{-9}$
BaC_2O_4	9.2×10^{-2}	4.1×10^{-4}	$[Ba] \times [C_2O_4] = 1.7 \times 10^{-7}$
$BaCrO_4$	3.8×10^{-3}	1.5×10^{-5}	$[Ba] \times [CrO_4] = 2.3 \times 10^{-10}$
BaF_2	1.3	7.5×10^{-3}	$[Ba] \times [F]^2 = 1.7 \times 10^{-6}$
$Ba(IO_3)_2$	2.5×10^{-1}	5.3×10^{-4}	$[Ba] \times [IO_3]^2 = 6.0 \times 10^{-10}$
$BaSO_4$	2.5×10^{-3}	1.1×10^{-5}	$[Ba] \times [SO_4] = 1.2 \times 10^{-10}$
$Ca(IO_3)_2$	2.1	5.4×10^{-3}	$[Ca] \times [IO_3]^2 = 6.5 \times 10^{-7}$
$CaCO_3$	1.3×10^{-2}	1.3×10^{-4}	$[Ca] \times [CO_3] = 1.7 \times 10^{-8}$
CaC_2O_4	5.7×10^{-3}	4.5×10^{-5}	$[Ca] \times [C_2O_4] = 2 \times 10^{-9}$
$CaCrO_4$	23.	1.5×10^{-1}	$[Ca] \times [CrO_4] = 2.3 \times 10^{-2}$
$CaC_4H_4O_6$ (tartrate)	1.7×10^{-1}	8.8×10^{-4}	$[Ca] \times [C_4H_4O_6] = 7.7 \times 10^{-7}$
CaF_2	1.6×10^{-2}	2.0×10^{-4}	$[Ca] \times [F]^2 = 3.2 \times 10^{-11}$
$CaSO_4$	1.1	7.8×10^{-3}	$[Ca] \times [SO_4] = 6.1 \times 10^{-5}$
CdC_2O_4	2.0×10^{-2}	1.0×10^{-4}	$[Cd] \times [C_2O_4] = 1.1 \times 10^{-8}$
CdS	8.6×10^{-13}	6.0×10^{-15}	$[Cd] \times [S] = 3.6 \times 10^{-29}$
$Ce_2(C_4H_4O_6)_3$ (tartrate)	4.4×10^{-2}	6.1×10^{-5}	$[Ce]^2 \times [C_4H_4O_6]^3 = 9.7 \times 10^{-20}$
$Ce_2(C_2O_4)_3$	4.1×10^{-4}	7.5×10^{-7}	$[Ce]^2 \times [C_2O_4]^3 = 2.6 \times 10^{-29}$
$Ce(IO_3)_3$	1.3	1.9×10^{-3}	$[Ce] \times [IO_3]^3 = 3.5 \times 10^{-10}$
$Co(OH)_2$	5.5×10^{-5}	7.4×10^{-7}	$[Co] \times [OH]^2 = 1.6 \times 10^{-18}$
CoS	1.6×10^{-12}	1.7×10^{-13}	$[Co] \times [S] = 3 \times 10^{-26}$
$Cu_2(CNS)_2$	5.0×10^{-4}	2.1×10^{-6}	$[Cu] \times [CNS] = 1.7 \times 10^{-11}$
Cu_2Br_2	2.9×10^{-2}	1.0×10^{-4}	$[Cu] \times [Br] = 4.1 \times 10^{-8}$
Cu_2Cl_2	1.2×10^{-1}	6.0×10^{-4}	$[Cu] \times [Cl] = 1.4 \times 10^{-6}$
CuC_2O_4	2.6×10^{-2}	1.7×10^{-4}	$[Cu] \times [C_2O_4] = 2.9 \times 10^{-8}$
Cu_2I_2	3.0×10^{-4}	8.0×10^{-7}	$[Cu] \times [I] = 2.6 \times 10^{-12}$
$Cu(IO_3)_2$	3.0	7.2×10^{-3}	$[Cu] \times [IO_3]^2 = 1.4 \times 10^{-7}$
CuS	8.8×10^{-21}	9.2×10^{-23}	$[Cu] \times [S] = 8.5 \times 10^{-45}$
$Fe(OH)_2$	1.44×10^{-3}	1.6×10^{-5}	$[Fe] \times [OH]^2 = 1.6 \times 10^{-14}$
$Fe(OH)_3$	4.8×10^{-8}	4.5×10^{-10}	$[Fe] \times [OH]^3 = 1.1 \times 10^{-36}$
FeS	3.4×10^{-8}	3.9×10^{-10}	$[Fe] \times [S] = 1.5 \times 10^{-19}$
Hg_2Br_2	3.9×10^{-5}	6.9×10^{-8}	$[Hg_2] \times [Br]^2 = 1.3 \times 10^{-21}$
Hg_2Cl_2	3.8×10^{-4}	8.0×10^{-7}	$[Hg_2] \times [Cl]^2 = 2.0 \times 10^{-18}$
Hg_2I_2	2.0×10^{-7}	3.1×10^{-10}	$[Hg_2] \times [I]^2 = 1.2 \times 10^{-28}$
HgO	3.2×10^{-7}	1.5×10^{-9}	$[Hg] \times [OH]^2 = 1.4 \times 10^{-26}$
HgS	1.5×10^{-24}	6.3×10^{-27}	$[Hg] \times [S] = 4 \times 10^{-53}$
$KHC_4H_4O_6$	3.2	1.7×10^{-2}	$[K] \times [HC_4H_4O_6] = 3.0 \times 10^{-4}$
K_2PtCl_6	11.	2.3×10^{-2}	$[K]^2 \times [PtCl_6] = 4.9 \times 10^{-5}$

SOLUBILITIES AND SOLUBILITY PRODUCTS AT ROOM TEMPERATURE — *Continued*

Substance	Solubility in Grams per Liter	Solubility in Moles per Liter	Solubility Product
$La_2(C_2O_4)_3$	6.0×10^{-4}	1.1×10^{-6}	$[La]^2 \times [C_2O_4]^3 \times 2.0 \times 10^{-28}$
$La_2(C_4H_4O_6)_3$	5.2×10^{-2}	7.2×10^{-5}	$[La]^2 \times C_4H_4O_6]^3 = 2.0 \times 10^{-19}$
$La(IO_3)_3$	1.5	2.2×10^{-3}	$[La] \times [IO_3]^3 = 5.9 \times 10^{-10}$
$MgCO_3$	4.3×10^{-1}	5.1×10^{-3}	$[Mg] \times [CO_3] = 2.6 \times 10^{-5}$
MgC_2O_4	1.0	9.3×10^{-3}	$[Mg] \times [C_2O_4] = 8.6 \times 10^{-5}$
MgF_2	7.4×10^{-2}	1.2×10^{-3}	$[Mg] \times [F]^2 = 7.0 \times 10^{-9}$
$MgNH_4PO_4$	8.6×10^{-3}	6.3×10^{-5}	$[Mg] \times [NH_4] \times [PO_4] = 2.5 \times 10^{-12}$
$Mg(OH)_2$	4.9×10^{-3}	8.5×10^{-5}	$[Mg] \times [OH]^2 = 1.2 \times 10^{-11}$
$Mn(OH)_2$	1.9×10^{-3}	2.2×10^{-5}	$[Mn] \times [OH]^2 = 4.0 \times 10^{-14}$
MnS flesh colored	2.2×10^{-7}	2.6×10^{-6}	$[Mn] \times [S] = 7 \times 10^{-16}$
MnS green	2.2×10^{-9}	2.5×10^{-11}	$[Mn] \times [S] = 6.2 \times 10^{-22}$
$Ni(OH)_2$	5.6×10^{-5}	6.0×10^{-7}	$[Ni] \times [OH]^2 = 8.7 \times 10^{-19}$
NiS least soluble allotropic form	7.0×10^{-11}	1.2×10^{-12}	$[Ni] \times [S] = 1.4 \times 10^{-24}$
$PbBr_2$	9.7	2.7×10^{-2}	$[Pb] \times [Br]^2 = 7.9 \times 10^{-6}$
$PbCl_2$	11.0	3.9×11^{-2}	$[Pb] \times [Cl]^2 = 2.4 \times 10^{-4}$
$PbCO_3$	4.8×10^{-5}	1.8×10^{-7}	$[Pb] \times [CO_3] = 3.3 \times 10^{-14}$
PbC_2O_4	1.7×10^{-3}	5.8×10^{-6}	$[Pb] \times [C_2O_4] = 3.4 \times 10^{-11}$
$PbCrO_4$	4.3×10^{-5}	1.3×10^{-7}	$[Pb] \times [CrO_4] = 1.8 \times 10^{-14}$
PbF_2	2.9×10^{-1}	1.2×10^{-3}	$[Pb] \times [F]^2 = 7.0 \times 10^{-9}$
PbI_2	6.8×10^{-1}	1.5×10^{-3}	$[Pb] \times [I]^2 = 1.4 \times 10^{-8}$
$Pb(IO_3)_2$	1.6×10^{-2}	4.2×10^{-5}	$[Pb] \times [IO_3]^2 = 3.0 \times 10^{-13}$
$Pb_3(PO_4)_2$	1.4×10^{-4}	1.7×10^{-7}	$[Pb]^3 \times [PO_4]^2 = 1.5 \times 10^{-32}$
PbS	4.9×10^{-12}	2.0×10^{-14}	$[Pb] \times [S] = 4.2 \times 10^{-28}$
$PbSO_4$	4.5×10^{-2}	1.1×10^{-4}	$[Pb] \times [SO_4] = 1.1 \times 10^{-8}$
$SrCO_3$	5.9×10^{-3}	4.0×10^{-5}	$[Sr] \times [CO_3] = 1.6 \times 10^{-9}$
SrC_2O_4	4.4×10^{-2}	2.4×10^{-4}	$[Sr] \times [C_2O_4] = 5.6 \times 10^{-8}$
SrF_2	2.3×10^{-1}	1.8×10^{-3}	$[Sr] \times [F]^2 = 2.5 \times 10^{-9}$
$SrSO_4$	9.6×10^{-2}	5.3×10^{-4}	$[Sr] \times [SO_4] = 2.8 \times 10^{-7}$
TlBr	4.0×10^{-1}	1.4×10^{-3}	$[Tl] \times [Br] = 2.0 \times 10^{-6}$
$TlBrO_3$	3.0	9.1×10^{-3}	$[Tl] \times [BrO_3] \times 8.5 \times 10^{-5}$
TlCNS	3.2	1.2×10^{-2}	$[Tl] \times [CNS] = 1.4 \times 10^{-4}$
TlCl	3.4	1.4×10^{-2}	$[Tl] \times [Cl] = 2.0 \times 10^{-4}$
TlI	.....	1.7×10^{-4}	$[Tl] \times [I] = 2.8 \times 10^{-8}$
$TlIO_3$	5.7×10^{-1}	1.5×10^{-3}	$[Tl] \times [IO_3] = 2.2 \times 10^{-6}$
Tl_2S	2.9×10^{-6}	6.6×10^{-9}	$[Tl]^2 \times [S] = 1.2 \times 10^{-24}$
$Zn(OH)_2$	6.1×10^{-5}	6.3×10^{-7}	$[Zn] \times [OH]^2 = 1.0 \times 10^{-18}$
ZnS	3.3×10^{-10}	3.5×10^{-12}	$[Zn] \times [S] = 1.2 \times 10^{-23}$

The above table is prepared from many sources, and some of the values are based upon solubility determinations by methods which are now considered inaccurate.

The table gives a good idea, however, of the relative order of magnitude. For copper sulfide, the table states that 8.8×10^{-21} g dissolve in 1 l of water. Obviously, the experimental determination of such a small value is fraught with difficulty and the probable error is large. For most purposes such a value represents a negligible quantity, and the statement is often made that copper sulfide is insoluble in water. It is instructive, however, to compare the solubility products of the various sulfides, and important methods of separation have been based upon such studies. Only two significant figures have been given in the table, although it is obvious that more would be justifiable for the more soluble substances, though even the first figure is doubtful for the very insoluble substances. The values are affected to different degrees by changes in temperature and the presence of other substances in solution. A careful, critical study of all the experimental data would be necessary to give the proper number of significant figures, and it would be necessary to give the exact temperature.

In compiling the table some of the solubilities in grams per liter have been computed backward from the values found in the literature for the solubility products. In making these computations it has been assumed that the substances are completely ionized and no allowance is made for hydrolytic effects. Thus it is assumed that when water is saturated with calcium carbonate an equal number of calcium and carbonate ions are present in the saturated solution of calcium carbonate. As a matter of fact, however, there is a reaction between water and CO_3^{--} ions which results in the formation of HCO_3^- ions, and the OH^- concentration becomes greater than that of pure water, as is easy to show by tests with indicators: $CO_3^{--} + H_2O = HCO_3^- + OH^-$. As a result of this hydrolysis, more calcium carbonate dissolves than otherwise would, so that the value given in the table for the weight of $CaCO_3$ dissolved is too small if the solubility product is correct or, if the weight of salt dissolved is correct, then the value of the solubility product given in the table is too large. It is possible to compute the extent of hydrolysis from the ionization constants of water and of the acid and base composing any salt, but this computation is difficult because it involves the solving of a cubic equation containing more than one term. The common practice of neglecting hydrolysis in such a table is justifiable because the values are not known accurately enough to warrant the mathematical labor required to carry out the necessary computations that would be involved in making allowances for hydrolytic effects even although there is over 50 per cent hydrolysis as in the case of calcium carbonate.

The literature contains an account of a great deal of work concerning the solubilities of chemical compounds, and it is often difficult to reconcile some of the published values. Many of the values in the table are taken from the work of Kohlrausch, who, with his students, published a number of papers between 1890 and 1903. The Kohlrausch values were based upon measurements of the electrical conductivity of solutions obtained by keeping the salt in contact with water until equilibrium was reached. Böttger in 1903 published considerable data, and many of his results agreed well with values obtained by Kohlrausch. With these values, the solubility products can be computed from the solubility of the salts as will be explained.

In 1906, Weigel published the results of an extensive study of the solubilities of sulfides. His results were also based upon conductivity measurements, but in establishing the relation between the molar solubility and the solubility product, he assumed that the sulfides were completely hydrolyzed when dissolved.

The values obtained by Weigel compared with those of Kohlrausch and of Böttger showed that the solubility of sulfides of metals other than the alkalies and alkaline

earths is less than that of the common salts of low solubility. The Weigel values, however, do not account satisfactorily for the readiness with which the sulfides are formed from solutions of varying acidity. Weigel found, to be sure, that HgS is the least soluble sulfide but placed its solubility at 0.054×10^{-6} mole per liter. The solubility of ZnS was given as 70.6×10^{-6}, that of MnS as 71.6×10^{-6}, and that of FeS as 70.1×10^{-6}.

This does not agree very well with the facts known with respect to the precipitation of cations with hydrogen sulfide. There is not enough difference between the solubilities of HgS, the least soluble sulfide, and MnS, the most soluble sulfide of those obtained in qualitative analysis. It is not easy to see why HgS should be formed from very acid solutions whereas a very low concentration of acid serves to prevent any precipitation of MnS. The known fact that ZnS can be completely precipitated from a solution of low acidity in the presence of manganese ions, which are not precipitated, is also inexplicable because Weigel found MnS to be of about the same solubility as ZnS.

Bruner and Zawadski in 1909 made further studies of the solubilities of sulfides with the aid of the mass-action law and solubility-product principle. At this time, data were available concerning the primary and secondary ionization of hydrogen sulfide. With these new data, they recalculated the results obtained by some of the previous investigators. They found the solubility of HgS to be 3.2×10^{-24} or 2.8×10^{-27} by such recalculations, and their own value for MnS was 2.6×10^{-8}.

A similar state of contradiction prevails with respect to solubility determination of oxides and hydroxides. Values given by Remy and Kuhlmann in 1924-5 do not agree with those given by Britton in 1925. Thus Remy and Kuhlmann found that 1.8×10^{-5} mole of $Zn(OH)_2$ will dissolve in a liter of pure water, and the value given by Britton was 3.4×10^{-9}.

If one wishes to know how much of a precipitate will dissolve upon washing it with water, the values obtained by Weigel for the sulfides and by Remy and Kuhlmann for the hydroxides are undoubtedly more useful, but even their values may then appear somewhat low. On the other hand, if one wishes to predict whether a precipitation will take place or whether a separation can be made on the basis that one element will be precipitated and the other remain in solution, the values of Bruner and Zawadski are much better than those of Weigel for the sulfides, and those of Britton are better than those of Remy and Kuhlmann for the hydroxides. This latter purpose was in mind in preparing the above table.

Some examples will be given to illustrate the method of computing the molar solubility, S_m, and the solubility product, S_p. A saturated solution of silver iodide contains 3.0×10^{-6} g (= 0.0030 mg) per liter. The molecular weight of silver iodide is 234.8. The saturated solution, therefore, contains $\frac{3.0 \times 10^{-6}}{235} = 1.3 \times 10^{-8}$ mole per liter. At this dilution the dissolved silver iodide can be assumed to be completely ionized:

$$AgI \rightleftarrows Ag^+ + I^-$$

and since 1 mole of silver iodide furnishes 1 mole of silver ions and 1 mole of iodide ions, it is evident that the solubility product, S_p, is for

$$[Ag] \times [I] = [1.3 \times 10^{-8}] \times [1.3 \times 10^{-8}] = 1.7 \times 10^{-16} = S_p$$

A saturated solution of silver phosphate contains 6.5×10^{-3} g (= 6.5 mg) per liter. The substance is much more soluble in water than silver iodide, but its solubility product is smaller. The molecular weight of silver phosphate is 418.7. The

saturated solution, therefore, contains $\frac{6.5 \times 10^{-3}}{419} = 1.6 \times 10^{-5}$ mole of silver phosphate per liter, which can be assumed to be completely ionized:

$$Ag_3PO_4 \rightleftarrows 3\ Ag^+ + PO_4^{---}$$

1 mole of silver phosphate yielding 3 moles of silver* and 1 mole of phosphate ions. The solubility product is

$$[Ag]^3 \times [PO_4] = [3 \times 1.6 \times 10^{-5}]^3 \times [1.6 \times 10^{-5}] = 1.8 \times 10^{-18} = S_p$$

As a still more complicated case, let us consider lead phosphate. The solubility product, $[Pb]^3 \times [PO_4]^2$, is 1.5×10^{-32}. If x moles of $Pb_3(PO_4)_2$ dissolve in enough water to make a liter of solution and the salt is completely ionized, the solution will contain $3\ x$ moles of Pb^{++} and $2\ x$ moles of PO_4^{---}, and

$$108\ x^5 = 1.5 \times 10^{-32} = 1500 \times 10^{-35}$$
$$x^5 = 14. \times 10^{-35}$$
$$x = 1.7 \times 10^{-7}$$

The easiest way to get the fifth root of a number like 14×10^{-35} is with the aid of logarithms, remembering that the root of a product is the product of the roots of the individual terms.

The fifth root of 10^{-35} is 10^{-7}

$$\log 14 = 1.15$$
$$\tfrac{1}{5} \text{ of } 1.15 = 0.23 = \log \text{ of } 1.7$$

Hence if $x^5 = 14 \times 10^{-35}$, $x = 1.7 \times 10^{-7}$. If the power of 10 is not divisible by 5, make it so. Thus $\sqrt[5]{1.4 \times 10^{-34}} = \sqrt[5]{14 \times 10^{-35}}$.

The procedure for finding any other root is similar.

We have already seen that in connection with small hydrogen-ion concentrations it is convenient to use the "negative logarithm" of the number. Thus, instead of the solubility product, S_p, Kolthoff in his numerous publications uses the value $\log \frac{1}{S_p} = p_S$. If the solubility product of $Ag_3PO_4 = 1.8 \times 10^{-18}$, then $p_S = 17.74$. Such a value is less awkward than $0.0_{16}18$. In most countries except the United States one *billion* is defined as one million million and one-billionth is 10^{-12}. In the United States, one billion is a thousand million and one-billionth is 10^{-9}. Obviously this leads to confusion when one attempts to name very large or very small numbers. With the latter, this difficulty is overcome by using the negative logarithm.

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* If x moles of Ag_3PO_4 dissolve in enough water to make a liter of solution and the Ag_3PO_4 is completely ionized, the concentration of the Ag^+ is $3\ x$ and that of the PO_4^{---} is x when the concentration is expressed in *moles per liter*. If the concentration is expressed in *equivalents per liter* (*i.e.*, in terms of *normal* solutions), the x moles of Ag_3PO_4 furnish $3\ x$ equivalents of Ag_3PO_4 which ionize into $3\ x$ equivalents of Ag^+ and $3\ x$ equivalents of PO_4^{---}. The mass-action-law expression $\frac{[Ag]^3 \times [PO_4]}{[Ag_3PO_4]} = k$ *holds for any method of expressing concentrations, but it is, on the whole, simplest and best to express solubility products in moles per liter,* and $[Ag]^3 \times [PO_4] = 27\ x^4$ in a saturated solution of silver phosphate containing x *molecules of dissolved silver phosphate completely ionized. From the solubility product,* the quantity of dissolved substance can be calculated.

Salt Effect. It has already been pointed out (cf. page 12) that the mass-action law is inexact when the concentrations of the molecules or ions are taken as the "active masses." The more correct expression of the solubility product of a salt, BA, which forms the univalent ions B^+ and A^-, is

$$a_B \cdot a_A = S_{BA}$$

where a_B and a_A represent the activities of B^+ and A^- respectively. Since

$$a = cf$$

the mass-action law becomes

$$[B^+]\ [A^-] f_B \cdot f_A = S_{BA}$$

In this expression, S_{BA} is regarded as a true constant, but the activity coefficients are not. In solutions containing very little soluble salt, the values of f_B and f_A may be regarded as equal to unity, which means that the activity coefficients can be disregarded when a slightly soluble salt is present in pure water. If, however, an electrolyte is present in the solution which has no ion in common with the precipitate, the values of f_B and f_A decrease and

$$[B^+]\ [A^-] = \frac{S_{BA}}{f_B \cdot f_A}$$

which means that the solubility of a precipitate in a solution of an electrolyte which has no ion in common with the precipitate is greater than it is in pure water. This is what is known as the *salt effect;* it must not be confused with the "salting-out" effect which is sometimes obtained when considerable sodium chloride is added to a colloidal solution.

Some idea of the salt effect is shown by the fact that a solution of 0.01 N KNO_3 will dissolve 12 per cent more AgCl and 170 per cent more $BaSO_4$ than the same volume of pure water. Similarly, a 0.01 N NaCl solution will dissolve 60 per cent more calcium oxalate than pure water will. These values illustrate the fact that the effect of an added electrolyte containing no ion in common with a precipitate is greater as the valence of the ions of the precipitate increases; the effect also depends upon the nature of the electrolyte added.

Influence of Temperature on Solubility. If heat is absorbed and the solution becomes colder as the salt dissolves, raising the temperature will increase the solubility. This is in accordance with the theorem of Le Chatelier: *Any alteration in the factors which determine an equilibrium causes the equilibrium to be displaced in such a way as to oppose, as far as possible, the effect of the alteration.* Most precipitates are more soluble in hot water than in cold; this effect is very pronounced with silver chloride, of which 21 mg dissolve in 100 ml of boiling hot water and only 0.9 mg in the same volume of water at 10°.

Formation of Complex Ions

Silver chloride dissolves readily in dilute ammonia solution. The following reaction takes place:

$$AgCl + 2\ NH_3 \rightleftarrows Ag(NH_3)_2Cl$$

A study of the properties of this new substance shows that it dissociates in aqueous solution chiefly in this way:

$$Ag(NH_3)_2Cl \rightleftarrows [Ag(NH_3)_2]^+ + Cl^-$$

The ionic changes involved in the last two equations may be expressed thus:

$$AgCl \rightleftarrows Ag^+ + Cl^- \quad Ag^+ + 2\,NH_3 \rightleftarrows [Ag(NH_3)_2]^+$$

and, in accordance with the law of mass action, the greater the concentration of the ammonia, the greater the extent to which the reaction takes place in the direction left to right. In a normal solution of ammonia, the ratio of the concentration of the $[Ag(NH_3)_2]^+$ ion to that of the simple Ag^+ ion is about $10^7 : 1$. The $[Ag(NH_3)_2]^+$ ion does not give many reactions that the simple Ag^+ ion does. It is called a *complex* cation.

When potassium cyanide is added to silver nitrate solution a white precipitate of silver cyanide is formed: $CN^- + Ag^+ \rightleftarrows = AgCN$, but if an excess of potassium cyanide is used the precipitate dissolves

$$AgCN + CN^- \rightarrow [Ag(CN)_2]^-$$

and the silver has become a part of the anion. In this case the value of the ratio of complex ion to simple ion is even larger than in the case of the silver ammonia cation.

Similarly, when insoluble ferrous cyanide is treated with an excess of potassium cyanide, it dissolves, forming the ferrocyanide anion:

$$Fe(CN)_2 + 4\,CN^- \rightarrow [Fe(CN)_6]^{----}$$

This anion shows none of the ordinary reactions of ferrous ions.

It is, in fact, quite common to find that simple ions, particularly in concentrated solutions, are capable of forming such complex ions. The simple ions can unite with neutral molecules, or with ions of opposite charge, to form complex ions. If a simple ion adds to itself a neutral molecule, such as H_2O, H_2O_2, NH_3, or organic radicals, then neither the original valence nor the electric charge is changed. Thus the trivalent cobalt ion is capable of forming a deep red ion with 6 molecules of ammonia, and this complex ion has a trivalent charge like that of the original simple ion.

$$Co^{+++} + 6\,NH_3 \rightleftarrows [Co(NH_3)_6]^{+++}$$

If, in such a complex ion, one or more of the ammonia groups is replaced by a negative univalent ion, the valence of the complex ion is reduced one for each atom of negative ion thus entering into the complex

$$[Co(NH_3)_6]^{+++};\ [Co(NH_3)_5 \cdot NO_2]^{++};\ \left[Co\begin{matrix}(NO_2)_2\\(NH_3)_4\end{matrix}\right]^{+};\ \left[Co\begin{matrix}(NO_2)_3\\(NH_3)_3\end{matrix}\right]$$

Upon adding excess potassium cyanide to the solution, the trivalent cobalt ion unites with six CN^- ions to form a complex ion which, in accordance with the above rule, has a triple negative charge. *The valence or electric character of a complex ion is the algebraic sum of the valences or electric charges of the constituents.*

As already indicated, the stability of these complex ions varies. When the complex is very stable the common reactions of the constituents are not shown.

Besides these complex ions certain double salts are known. Thus potassium and aluminum sulfates crystallize together, forming an alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$.

When this salt is dissolved in water, the solution shows all the reactions for potassium, aluminum, and sulfate ions, and there is little evidence of the formation of a complex ion. To determine whether a given substance is a double salt or a complex salt, it is customary merely to see whether the characteristic reactions of the simple ions are shown. A salt exists which has the formula $KCr(C_2O_4)_2 \cdot 5\ H_2O$. An aqueous solution of this salt readily shows the reactions for potassium ions, but reacts sluggishly when tested for chromium cations or for oxalate anions. Evidently the chromium and the oxalate have united to form a complex anion with a negative valence of one, but this complex is not as stable as some of the others that have been mentioned. It is probable that there is no sharp distinction between the double salts and the complex salts, and probably the double salts are most logically to be classed as complex salts of which the complex ion is not very stable. As a general rule, those complex salts which are composed of neutral salts of strong acids yield complex anions which are largely dissociated into simple ions in dilute solution. On the other hand, complex ions composed of positive ions and anions of weak acids are usually very stable.

IONIZATION CONSTANTS OF CERTAIN COMPLEX IONS

$$\frac{[Ag^+] \times [NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8 \times 10^{-8} \qquad \frac{[HgCl_2]\,[Cl^-]^2}{[HgCl_4^{--}]} = 1.0 \times 10^{-2}$$

$$\frac{[Ag^+] \times [NO_2^-]^2}{[Ag(NO_2)_2^-]} = 1.5 \times 10^{-3} \qquad \frac{[Hg^{++}]\,[Cl^-]^4}{[HgCl_4^{--}]} = 6.0 \times 10^{-17}$$

$$\frac{[Ag^+]\,[S_2O_3^{--}]}{[AgS_2O_3^-]} = 1.0 \times 10^{-13} \qquad \frac{[Hg^{++}]\,[Br^-]^4}{[HgBr_4^{--}]} = 2.2 \times 10^{-22}$$

$$\frac{[Ag^+]\,[CN^-]^2}{[Ag(CN)_2^-]} = 1.0 \times 10^{-21} \qquad \frac{[Hg^{++}]\,[I^-]^4}{[HgI_4^{--}]} = 5.0 \times 10^{-31}$$

$$\frac{[Cu^+]\,[CN^-]^4}{[Cu(CN)_4^{---}]} = 5.0 \times 10^{-28} \qquad \frac{[Hg^{++}]\,[CNS^-]^4}{[Hg(CNS)_4^{--}]} = 1.0 \times 10^{-22}$$

Reactions of the Ions

As already indicated, most of the reactions used in qualitative analysis involve reactions between ions. We have seen that, in principle, all reactions are reversible and have learned to understand some of the laws which govern these reversible reactions. In analytical chemistry, it is necessary for the most part to employ reactions which take place almost completely in the desired direction. Unless a reaction can be made to go nearly to completion in a given direction, it is of little value either as a sensitive test or for furnishing a method of separation. The useful reactions of qualitative analysis, namely, those which apparently go to completion, may be brought into four classes:

1. Reactions in which a gas is formed.
2. Reactions in which a precipitate is formed.
3. Reactions in which a non-ionized substance is formed.
4. Reactions of oxidation and reduction.

If a gas is formed as a result of a chemical reaction, usually all the gas can be boiled out of solution, and thus all reactions of this type can be made to go to completion. The reaction can be stopped by preventing the escape of the gas; this shows that the reaction is inherently a reversible one.

Whenever a substance which has a very small solubility product is formed by means of a chemical reaction, the greater part of the substance will leave the solution in the form of a precipitate and the reaction will go practically to completion. The table on page 21 shows that the saturated solution of silver chloride contains only about one hundred-thousandth of a mole (= 0.01 millimole) of solid salt per liter. The table also shows that when the product obtained by multiplying the concentration of the silver ions by the product of the concentration of the chloride ions in an aqueous solution is equal to 1.2×10^{-10} the solution is saturated with silver chloride. By adding an excess of chloride ions to a solution containing silver ions, it is possible, therefore, to precipitate nearly all the silver. It is evident that it will take less silver ions to give the solubility product when an excess of chloride ions is used than when pure silver chloride is dissolved in water.

The precipitated silver chloride will dissolve completely in potassium cyanide, because the silver ion forms with the cyanide ion a complex ion $[Ag(CN)_2]^-$ which is ionized to such a slight extent that the solubility product of silver chloride is no longer reached, even although all the chlorine is present in the ionic condition. AgCl also dissolves in strong HCl or NaCl solutions, probably forming $[AgCl_2]^-$ anions.

The formation of a non-ionized substance also causes a reaction to go to completion. The table on page 11 shows the ionization values of a few common substances. This table may be used exactly like that of the solubility products to enable one to predict whether a reaction is likely to go in a given direction. The equilibrium between water and its ions H^+ and OH^- has been discussed on page 17. The same reasoning may be applied to the equilibrium between any other slightly ionized substance and its ions; whenever the ions are added separately to a solution, some of the non-ionized substance is at once formed. Thus when any acid is added to the solution of a sulfide a reaction takes place, partly because the hydrogen sulfide is a very weak electrolyte and partly because the substance is a gas. Similarly calcium phosphate dissolves in hydrochloric acid because more PO_4^{---} ions are formed from dissolved calcium phosphate than are formed from $H_2PO_4^-$ ions in the presence of an excess of H^+ ions from the hydrochloric acid; the reaction takes place because of the formation of a non-ionized substance.

Finally, many reactions of oxidation and reduction take place nearly to absolute completion, although all these reactions can be shown to be inherently of a reversible type. To understand such equilibria, however, it is necessary to discuss oxidation and reduction at greater length.

Oxidation and Reduction

The term *oxidation*, in its narrowest sense, signifies the taking up of oxygen by an element or compound. Thus ferrous oxide, on being heated in the air, is converted into ferric oxide, and the reaction is called an oxidation. Since, however, ferric chloride bears the same relation to ferrous chloride that ferric oxide bears to ferrous oxide, it is customary to call the change of ferrous chloride into ferric chloride an oxidation,

although it is not necessary to think that oxygen takes part in the reaction at all. This is an interesting example of a word in common use which has come to mean a great deal more than it originally meant. Indeed, chemists have departed so far from the original meaning of *oxidation* that sometimes the word seems inappropriate, and the use of another word, such as *adduction*, has been suggested. Reduction is the exact opposite to oxidation, and whenever one substance is oxidized some other substance is reduced. Hydrogen was formerly considered to be the typical reducing agent, so that the definition for oxidation used to read something like this: Oxidation is the addition of oxygen (or its equivalent) to an element or compound or the taking away of hydrogen (or its equivalent).

The reaction between ferrous chloride and chlorine:

$$2\,FeCl_2 + Cl_2 \rightarrow 2\,FeCl_3$$

expressed in terms of the ionic theory becomes

$$2\,Fe^{++} + Cl_2 \rightarrow 2\,Fe^{+++} + 2\,Cl^-$$

In other words, the bivalent ferrous ion has been converted to trivalent ferric ion, and the neutral chlorine molecule has become changed to negatively charged chloride ions. In all other reactions in which a ferrous salt is oxidized, the valence of the iron is increased one, and the modern conception of oxidation and reduction is summed up very simply as follows:

Oxidation involves the loss of one or more electrons from an atom or ion whereby the apparent valence is increased in the positive direction; reduction is the gain of one or more electrons by an atom or ion whereby the apparent valence of the element or ion is changed in the opposite direction.

According to the electronic conception of the constitution of matter, the atom of an element consists of positively charged *protons*, *neutrons*, and negatively charged *electrons*. The mass associated with the positive electricity is much larger than that with the equal charge of negative electricity; the electrons are generally regarded as merely charges of negative electricity. The number of protons plus neutrons which make up the atom is probably a very small multiple of the atomic weight of the element. The originally neutral atom which loses an electron thus becomes positively charged and the atom which accepts the negatively charged electron becomes negatively charged, and a tube of force holds the two elements together in a so-called chemical compound. In the light of the electron theory, therefore, an element is oxidized when it loses an electron and an element is reduced when it receives an electron. This is the simplest, and at the same time most comprehensive, theory of oxidation that has ever been suggested.

Oxidation, according to this conception, is essentially an electric phenomenon. This theory suggests the thought that it ought to be possible to accomplish oxidation and reduction simply by means of electric energy. As a matter of fact, innumerable

reactions of oxidation and reduction can be made to take place in the electrolytic cell. Using the conventional symbol e to designate a unit charge of negative electricity and bearing in mind that the negative electricity is alone transferred and that the only way an element can gain in positive charge is by losing one or more negative electrons, we may express oxidations in the electrolytic cell as follows:

$$Fe^{++} - e \rightarrow Fe^{+++}$$

Such oxidations take place at the electrode called the anode. Conversely, at the cathode, ferric salts can be reduced to the ferrous condition:

$$Fe^{+++} + e \rightarrow Fe^{++}$$

Not only may all oxidations and reductions be accomplished by the electric current, but, vice versa, an electric current may be produced by a proper arrangement of the components of any reaction of oxidation and reduction. Thus some ferric chloride and sodium chloride solution in a small beaker may be connected with a second beaker containing sodium chloride by means of a U-tube filled with dilute salt solution. If a platinum electrode is placed in each beaker and the terminals are connected with a sensitive voltmeter, no current will pass through the wire. On pouring some hydrogen sulfide water into the beaker containing sodium chloride, a decided deflection of the voltmeter needle is at once observed, showing the passage of electricity. The negative electricity enters the voltmeter from the solution containing the hydrogen sulfide and passes on to the ferric chloride solution and back, through the *salt bridge*, to the hydrogen sulfide solution.* The chemical reaction that takes place is

$$2\ Fe^{+++} + S^{--} \rightarrow 2\ Fe^{++} + S$$

The electric current is produced as a result of the oxidation of the sulfide ions and reduction of the ferric ions.

Oxidation and reduction reactions are inherently reversible reactions, like all other chemical reactions, and are affected by the concentrations of the reacting substances. Thus, in the above experiment the intensity of the electric current can be greatly increased by using a soluble sulfide instead of hydrogen sulfide, the former being more largely dissociated and yielding a larger concentration of sulfide ions. Or, by adding a fluoride to the solution of ferric chloride, a fairly stable complex ion, $[FeF_6]^{---}$, is formed and the current slackens, owing to the decreased concentration of the ferric ions.

Some of the more important oxidizing agents used in analytical chemistry are the *halogens, nitric acid, potassium permanganate, potassium dichromate, hydrogen peroxide,* and *sodium peroxide.*

Important reducing agents are *metals, sulfurous acid, hydrogen sulfide, ferrous salts, titanous chloride, stannous chloride,* and *hydriodic acid.*

The oxidizing action of halogens depends upon the conversion of the neutral halogen into halide anions.

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* The conventional method of designating the direction in which a current flows is by means of an arrow pointing in the $+ \rightarrow -$ direction. According to the present theory, the current actually represents a flow of electrons in the direction opposite to that shown by the conventional arrow.

The oxidizing action of halogen upon ferrous ions results in the formation of ferric ions and of halide ions:

$$2\,Fe^{++} + Cl_2 \rightarrow 2\,Fe^{+++} + 2\,Cl^-$$

The action of halogen upon hydrogen sulfide is interesting. First of all, the sulfide ion is oxidized to free sulfur,

$$H_2S + Br_2 \rightarrow 2\,H^+ + 2\,Br^- + S$$

but, if the bromine is fairly concentrated, the reaction may go farther and the sulfur be converted into sulfuric acid; the whole reaction is then

$$H_2S + 4\,Br_2 + 4\,H_2O \rightarrow SO_4^{--} + 8\,Br^- + 10\,H^+$$

It will be noticed that it is very easy to balance equations of oxidation and reduction by noticing the change in valence. In this last equation sulfur goes from a negative valence of two to a positive valence of six, making an algebraic change of eight, which corresponds to the loss of eight electrons by the sulfur atom and the taking up of eight electrons by neutral bromine molecules.

The oxidizing action of nitric acid depends upon the reduction of the nitrogen. The extent of the reduction depends upon the concentration of the nitric acid and the nature of the substance oxidized. The more concentrated the nitric acid, the less it is reduced; the more concentrated the reducing agent and the stronger its reducing power the greater the reduction of the nitric acid. Nitric oxide, NO, is commonly formed, but often other products such as nitrogen dioxide, nitrous oxide, nitrogen, and even ammonia are produced.

In nitric acid, the nitrogen atom has five positive electric charges residing upon it. When it is reduced to nitric oxide, NO, it has only two positive charges, the nitrogen having accepted three electrons. The reaction between a ferrous salt and nitric acid is

$$3\,Fe^{++} + NO_3^- + 4\,H^+ \rightarrow 3\,Fe^{+++} + NO + 2\,H_2O$$

The action of nitric acid on a sulfide is interesting. If the nitric acid solution is cold and dilute (0.3 *N*) there is hardly any oxidation of the sulfur:

$$MnS + 2\,H^+ \rightarrow Mn^{++} + H_2S\uparrow$$

If the nitric acid is more concentrated (*e.g.*, 2 *N*) and the solution is heated, the sulfur of the sulfide is oxidized to free sulfur. Thus, for the reaction between copper sulfide and hot nitric acid, each atom of sulfur loses two electrons, and, in accomplishing the oxidation, an atom of nitrogen gains three electrons. The reaction may be expressed thus:

$$3\,CuS + 8\,H^+ + 2\,NO_3^- \rightarrow 3\,Cu^{++} + 4\,H_2O + 3\,S + 2\,NO$$

If the nitric acid is very concentrated, the greater part of it is reduced only to NO_2 and the sulfur is oxidized to sulfuric acid. The reaction may then be written:

$$CuS + 8\,H^+ + 8\,NO_3^- \rightarrow Cu^{++} + SO_4^{--} + 8\,NO_2 + 4\,H_2O$$

The oxidizing action of permanganate depends upon the readiness with which the MnO_4^- is converted into a manganese compound of lower valence. In the permanganate anion, MnO_4^-, the manganese has a positive valence of seven.* Ordinarily, in acid solution, the permanganate is reduced to bivalent manganese cation, corresponding to a loss of five positive charges, or acceptance of five electrons:

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ \rightarrow Mn^{++} + 5\,Fe^{+++} + 4\,H_2O$$
$$2\,MnO_4^- + 5\,H_2S + 6\,H^+ \rightarrow 2\,Mn^{++} + 5\,S + 8\,H_2O$$
$$2\,MnO_4^- + 5\,Sn^{++} + 16\,H^+ \rightarrow 2\,Mn^{++} + 5\,Sn^{++++} + 8\,H_2O$$
$$2\,MnO_4^- + 10\,HI + 6\,H^+ \rightarrow 2\,Mn^{++} + 5\,I_2 + 8\,H_2O$$

The oxidizing action of a chromate or dichromate ordinarily depends upon the formation of trivalent chromic ions. In the chromate and dichromate ions the chromium atom has a positive valence of six, so that for each atom of chromium the reduction corresponds to a loss of three positive charges, or gain of three electrons. Potassium chromate in acid solution is in equilibrium with the dichromate:

$$2\,CrO_4^{--} + 2\,H^+ \rightleftarrows 2\,HCrO_4^- \rightleftarrows H_2O + Cr_2O_7^{--}$$

In balancing equations, therefore, it makes little difference whether we start with the chromate or dichromate, except with respect to the quantity of acid required:

$$Cr_2O_7^{--} + 6\,Fe^{++} + 14\,H^+ \rightarrow 2\,Cr^{+++} + 6\,Fe^{+++} + 7\,H_2O$$
$$Cr_2O_7^{--} + 3\,S^{--} + 14\,H^+ \rightarrow 2\,Cr^{+++} + 3\,S + 7\,H_2O$$
$$Cr_2O_7^{--} + 3\,Sn^{++} + 14\,H^+ \rightarrow 2\,Cr^{+++} + 3\,Sn^{++++} + 7\,H_2O$$
$$Cr_2O_7^{--} + 6\,I^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 3\,I_2 + 7\,H_2O$$

Hydrogen peroxide acts both as an oxidizing agent and as a reducing agent. It oxidizes ferrous to ferric ions and it is capable of reducing permanganate to manganous salt. This anomalous behavior has been the cause of considerable discussion in the literature. It is unnecessary to go into the details of such a discussion, but a simple explanation of

* Note that the charge on an ion, such as MnO_4^-, is always the algebraic sum of the charges of its components. Seven of the negative charges of the four atoms of bivalent oxygen have been neutralized by the 7-valent Mn leaving one negative charge for the MnO_4^-.

this behavior will be suggested. In most compounds of hydrogen and oxygen, hydrogen has a positive valence of one and oxygen a negative valence of two. With hydrogen peroxide, also, it is best to assume that the hydrogen has its normal valence corresponding to one positive charge. If, then, the hydrogen has the positive valence of one, the O–O group in the H–O–O–H molecule has a valence of two toward hydrogen. In other words, the linkage of two atoms of the same kind together mutually satisfies one valence of each atom. Such a valence bond is called a *covalence* bond as there is no evidence of polarity between the two O–H groups in HO–OH.

When H–O–O–H acts as an oxidizing agent the bivalent –O–O– group is changed to H_2O in which we assume that the oxygen has a negative valence of two and bivalent –O–O– has been changed to two atoms of bivalent oxygen, which corresponds to two reducing units

$$2\,Fe^{++} + H_2O_2 + 2\,H^+ \rightarrow 2\,Fe^{+++} + 2\,H_2O$$

The reducing power of hydrogen peroxide also depends on the presence of the –O–O– group. To convert –O–O– (which group has a negative valence of two) to O_2 requires the transfer of two electrons to some other element. When an oxidizing agent such as MnO_4^-, MnO_2, or Co_2O_3 acts upon H_2O_2 in the presence of acid, one molecule of O_2 is liberated from each molecule of H_2O_2 and the liberated two electrons are taken up by the manganese or cobalt, thus causing the reduction of these elements.

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,O_2$$
$$MnO_2 + H_2O_2 + 2\,H^+ \rightarrow Mn^{++} + 2\,H_2O + O_2$$
$$Co_2O_3 + H_2O_2 + 4\,H^+ \rightarrow 2\,Co^{++} + 3\,H_2O + O_2$$

The characteristic action of the more important oxidizing agents has now been considered briefly; it remains to describe the characteristic behavior of the important reducing agents. Since every oxidation involves a simultaneous reduction, all the above reactions can be used to illustrate reduction as well as oxidation.

The reducing action of hydrogen and of metals depends upon the conversion of the neutral hydrogen* or metal into positively charged cations. Such a reduction may take place in acid, alkaline, or neutral solution.

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* Formerly, before the theory of oxidation and reduction potentials was known, it was customary to refer many of the reductions taking place in aqueous solution to the action of *nascent hydrogen*. Nascent hydrogen was the name given to hydrogen in the state in which it exists at the moment it is set free from a compound.

In the older nomenclature, the reducing action of sulfurous acid was attributed per-

(*a*) In acid solution, by the employment of zinc, etc.:

$$Zn + 2\,H^+ \rightarrow Zn^{++} + H_2\uparrow$$

This reaction in itself represents both an oxidation and a reduction, inasmuch as the metallic zinc, which is electrically neutral, becomes changed into zinc with two positive charges and, on the other hand, the hydrogen ions from sulfuric acid have each lost one positive charge and become electrically neutral hydrogen gas.

If some other ion easier to reduce than the hydrogen ion is present in the solution it is possible that no hydrogen will be evolved. Thus zinc can be amalgamated so that it will not react with acid and yet will reduce ferric ions to the ferrous condition:

$$2\,Fe^{+++} + Zn \rightarrow Zn^{++} + 2\,Fe^{++}$$

By the action of zinc and very dilute sulfuric acid, it is easy to transform silver chloride into metallic silver:

$$2\,Ag^+ + Zn \rightarrow Zn^{++} + 2\,Ag$$

or an arsenite into arsine:

$$H_2AsO_3^- + 3\,Zn + 7\,H^+ \rightarrow 3\,Zn^{++} + 3\,H_2O + AsH_3\uparrow$$

The result of this last equation is the oxidation of zinc from the metallic condition to the bivalent state and the reduction of the arsenic which is given three negative charges in place of the three positive charges it has in $H_2AsO_3^-$. Thus each As atom loses six positive charges and each Zn atom gains two, so that it takes three Zn atoms to reduce one $H_2AsO_3^-$ anion.

(*b*) In alkaline solution, by means of zinc, aluminum, sodium amalgam, or by Devarda's alloy (Cu = 50, Zn = 5, Al = 45):

$$Zn + 2\,OH^- \rightarrow ZnO_2^{--} + H_2\uparrow$$

$$2\,Al + 2\,OH^- + 2\,H_2O \rightarrow 2\,AlO_2^- + 3\,H_2\uparrow$$

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haps to the "affinity" that this substance had for oxygen. If the oxygen was obtained from water, then the hydrogen at the moment it was set free was assumed to be capable of causing reductions which hydrogen could not ordinarily accomplish. Similarly, when zinc reacts with dilute acid, hydrogen is evolved, and because zinc in the presence of dilute acid will accomplish reductions which hydrogen in its normal condition was incapable of effecting, it was customary to consider the action of zinc and acid as being due to *nascent hydrogen*.

The reducing power of an element, however, is determined by its specific oxidation potential (cf. p. 46). The higher the element stands in the electromotive series, the more easily it is oxidized and the greater is its power as a reducing agent. In general, today, the use of the term *nascent hydrogen* is unnecessary.

With Devarda's alloy the reaction is completed much more quickly than by the use of either zinc or aluminum alone. Nitrates and chlorates may be reduced in a few minutes by means of Devarda's alloy and a few drops of sodium hydroxide; the reaction also takes place in neutral solution, but it takes considerably longer:

$$NO_3^- + 4\,Zn + 7\,OH^- \rightarrow 4\,ZnO_2^{--} + 2\,H_2O + NH_3$$
$$ClO_3^- + 3\,Zn + 6\,OH^- \rightarrow 3\,ZnO_2^{--} + 3\,H_2O + Cl^-$$

In the nitrate ion nitrogen has a positive valence of five; in ammonia it has a negative valence of three. By the reduction with zinc, therefore, the nitrogen loses eight positive charges, or accepts eight electrons. At the same time the zinc loses two electrons, forming, in a neutral or alkaline solution, the zincate anion. Thus one atom of nitrogen in the nitrate ion requires four atoms of zinc to convert it into ammonia.

Similarly, the chlorine atom in the *chlorate ion* has a positive valence of five and is reduced to a negative valence of one by the reaction with zinc in neutral or alkaline solution. Thus one chlorate ion reacts with three atoms of zinc. Inspection of the above equilibrium expressions shows that one could predict that the reactions would take place best in alkaline solution in accordance with the mass-action law.

Reduction by means of sulfurous acid takes place in moderately acid solution and depends upon the fact that sulfur is more stable when it has six positive charges, as in sulfuric acid, than when it has only four as in sulfurous acid. Ferric salts are readily reduced by this reagent, and since the ferric ion gains only one electron while the sulfur atom loses two, it is evident that one molecule of sulfur dioxide (the anhydride of sulfurous acid) will reduce two atoms of iron in a ferric salt:

$$2\,Fe^{+++} + SO_3^{--} + H_2O \rightarrow 2\,Fe^{++} + SO_4^{--} + 2\,H^+$$

In a similar manner, the arsenate ion and many other substances are reduced very readily by means of SO_2 or SO_3^{--}:

$$H_2AsO_4^- + SO_3^{--} \rightarrow H_2AsO_3^- + SO_4^{--}$$

An excess of aqueous sulfurous acid is added to the solution which is to be reduced; it is then heated to boiling; and the boiling is continued while a stream of carbonic acid gas is passed through the solution until the excess of sulfurous acid is driven off.

Reduction by means of hydrogen sulfide, in which the sulfur atom possesses two negative charges, depends upon its oxidation to free sulfur, which is electrically neutral. Thus two atoms of ferric iron are reduced to ferrous iron by one molecule of hydrogen sulfide, and one molecule

of potassium dichromate reacts with three molecules of hydrogen sulfide:

$$2\,Fe^{+++} + H_2S \rightarrow 2\,Fe^{++} + 2\,H^+ + S$$

$$Cr_2O_7^{--} + 3\,H_2S + 8\,H^+ \rightarrow 2\,Cr^{+++} + 3\,S + 7\,H_2O$$

One objection to the use of hydrogen sulfide as a reducing agent is the difficulty involved in the subsequent removal of the precipitated sulfur by filtration. Moreover, hydrogen sulfide is used in qualitative analysis chiefly as a precipitant. If a solution contains an oxidizing agent (such as nitric acid, chloric acid, chromic acid, etc.), the sulfide ion will be oxidized and there will be separation of sulfur. Any sulfide obtained will be largely contaminated with sulfur, which renders the subsequent examination more difficult. If the solution contains no metal which is precipitated by hydrogen sulfide, but contains oxidizing agents, it will still cause separation of sulfur. One is often in doubt whether there is not some sulfide mixed with the sulfur, and is therefore obliged to examine the precipitate further, which is often unnecessary if the oxidizing agent is previously destroyed. Hydrogen sulfide reduces

Halogens:	$H_2S + Cl_2$	$\rightarrow 2\,H^+ + 2\,Cl^- + S$
Nitric acid:	$2\,H^+ + 2\,NO_3^- + 3\,H_2S$	$\rightarrow 4\,H_2O + 2\,NO\uparrow + S$
Chloric acid:	$ClO_3^- + 3\,H_2S$	$\rightarrow Cl^- + 3\,H_2O + 3\,S$
Ferric salts:	$2\,Fe^{+++} + H_2S$	$\rightarrow 2\,Fe^{++} + 2\,H^+ + S$
Dichromate	$Cr_2O_7^{--} + 3\,H_2S + 8\,H^+$	$\rightarrow 7\,H_2O + 2\,Cr^{+++} + 3\,S$
Permanganate:	$2\,MnO_4^- + 5\,H_2S + 6\,H^+$	$\rightarrow 8\,H_2O + 2\,Mn^{++} + 5\,S$

and many other substances.

Reduction with stannous chloride takes place usually in acid solutions. The reduction depends upon the fact that stannous ions are readily changed to stannic ions:

$$Sn^{++} + Cl_2 \rightarrow Sn^{++++} + 2\,Cl^-$$

or

$$SnCl_4^{--} + Cl_2 \rightarrow SnCl_6^{--}$$

Ferric salts, chromates, permanganates, mercuric salts, and many others are reduced in this way:

$$2\,Fe^{+++} + Sn^{++} \rightarrow 2\,Fe^{++} + Sn^{++++}$$

$$2\,CrO_4^{--} + 3\,Sn^{++} + 16\,H^+ \rightarrow 2\,Cr^{+++} + 3\,Sn^{++++} + 8\,H_2O$$

$$2\,HgCl_2 + Sn^{++} \rightarrow Sn^{++++} + Hg_2Cl_2 + 2\,Cl^-$$

$$Hg_2Cl_2 + Sn^{++} \rightarrow Sn^{++++} + 2\,Hg + 2\,Cl^-$$

$SnCl_2$ and $SnCl_4$ hydrolyze readily and form precipitates so that HCl is always added, and probably $SnCl_4^{--}$ and $SnCl_6^{--}$ are formed rather than Sn^{++} and Sn^{++++} in all these reactions.

Reduction with hydriodic acid depends upon the change of the iodine anion into free iodine. Most substances that are capable of being oxidized or reduced readily can be made to react with either hydriodic acid or with free iodine. It is easy to detect the presence of free iodine, and for this reason the iodometric reactions are extremely important in the study of analytical chemistry. To prevent the oxidizing effect of free iodine, an excess of potassium iodide is usually required, and means are often taken to remove the iodine as fast as it is formed; this is in accordance with the mass-action principle.

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,I_2$$

$$Cr_2O_7^{--} + 6\,I^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 7\,H_2O + 3\,I_2$$

$$2\,Fe^{+++} + 2\,I^- \rightarrow 2\,Fe^{++} + I_2$$

Electromotive Series and Electrode Potentials

If a substance like sugar lies as a solid on the bottom of a beaker filled with water, the molecules of sugar tend to distribute themselves throughout the solution; in other words, the sugar dissolves. The tendency of the solid molecules to pass into solution may be regarded as the result of pressure and, in fact, it is customary to say that the solid substance possesses a *solution pressure.*

If sufficient solid is present, eventually, with the aid of diffusion, the liquid will reach a state of saturation. The liquid then contains an equal quantity of sugar in all its parts and, at the prevailing temperature, will not dissolve any more sugar. There must, therefore, be some force which acts in opposition to the solution pressure and prevents a saturated solution from dissolving any more of the solid substance. This force is the *osmotic pressure* which the dissolved molecules exert in the solution. In a saturated solution, the osmotic pressure, which is itself determined solely by the number of molecules of dissolved substance and the temperature, exactly balances the solution pressure of the solid substance. The process of dissolving a solid substance involves no electrical effects. This is also true when the dissolved substance is an ordinary electrolyte, because an equal number of positive and negative ions is formed and there is no electric disturbance.

The metals themselves, though usually to a much less degree, also show a tendency to dissolve when placed in contact with water. In this case, however, an oxidation takes place, for, to the extent that it dissolves, the metal is converted into electrically charged ions. The tendency of the metal to dissolve is called its *electrolytic solution pressure.* Just as in the case of the sugar, the osmotic pressure of the dissolved ion

acts against the solution pressure. The electrolytic solution pressure has a definite value which is characteristic of each metal.

If a metal such as zinc, which oxidizes fairly readily, is placed in a *saturated* solution of zinc sulfate, none of the metal dissolves. If it is placed in contact with a *dilute* solution of zinc sulfate, the solution pressure of the zinc is greater than the deposition pressure and some positively charged zinc ions pass into solution. Thereby, the metal itself acquires a negative charge and the solution a positive charge. As a result of the charge residing upon the zinc ions that have gone into solution, an electrostatic force is produced which seeks to force the ions back upon the metal. This electromotive force is added to the osmotic pressure of all the zinc ions in solution and it increases rapidly with the number of ions that dissolve from the metal. When the sum of the osmotic pressure plus the electromotive force is equal to the electrolytic solution pressure of the zinc, the zinc stops dissolving.

When a less-readily oxidizable metal, such as copper, is placed in a copper sulfate solution the relations are reversed. In this case, except in extremely dilute solutions, the osmotic pressure is greater than the solution pressure and the metal does not dissolve; on the contrary, a few of the copper ions are discharged on the metal, giving to it a positive charge while the solution becomes negatively charged. Equilibrium is established as soon as a few of the ions have been thus deposited.

The potential difference between the metal and its solution, or, as it may be called, the electrode potential of the metal, is said to be negative when the charge of the solution is positive; this is the case with the readily oxidizable metals such as magnesium, aluminum, zinc, iron, etc. On the other hand, the electrode potential of the metal is positive when it is difficultly oxidizable; this is the case with copper, silver, platinum, and gold.

In previous editions of this book, the electrode potentials were called *reduction potentials*, but the above definition of positive and negative potentials applies to *oxidation potentials*.

In tables of electrode potentials, the alkali metals are invariably placed at the top, and since the chemist thinks of the alkali metals as *positive* with respect to other metals, it seems natural to assign a positive value to their electrode potentials. In an electric circuit, such as that obtained with the Daniell cell in which one electrode is copper in a solution of copper sulfate and the other electrode is zinc in a solution of zinc sulfate, the positive to negative direction (which is the reverse of the electron flow) is from the copper to the zinc *in the wire* and from zinc to copper *in the cell*. The decision, therefore, is purely arbitrary whether copper is regarded as positive or negative to zinc, for it depends upon whether one is thinking of the wire or of the electrolyte. The chemist naturally thinks of the solution, and the physicist thinks of the wire. This leads to confusion, and the numerical values in the tables of

electrode potentials are given sometimes with negative signs above hydrogen (arbitrarily taken as 0) and sometimes with positive signs. This matter has been referred to an international committee of scientists who have recommended that elements above hydrogen be given a negative sign in the table of electrode potentials. These electrode potentials are often called *oxidation potentials* and since reduction is the opposite to oxidation, some chemists persist in regarding zinc as positive to copper but call the table one of reduction potentials. This practice was followed in previous editions of this book to conform with the wishes of some of the writer's colleagues. Since most textbooks have adopted the nomenclature of the physicists and readers of this text may wish to consult other books, it seems best to define the electrode potentials in the conventional way.

Simple contact of a metal with a solution of its ions usually results in a potential difference between the metal and the solution. Such a potential is determined by the relation that exists between the electrolytic solution pressure of the metal and the osmotic pressure of the solution. Equilibrium is soon reached in most cases and the simple contact of a metal with a solution of its ions is not a permanent source of electricity. If, however, two metals of different potential are placed in contact with their respective solutions, and the two solutions are in electrolytic contact with one another, then electric charges of different potentials result, and if the two metals are connected outside the liquids by a wire, an electric current flows from the higher potential to the lower. Since the original differences in potential between the solutions and the metals are constantly being reëstablished, a permanent current results. This is the principle of the Daniell cell, in which a normal solution of copper sulfate is separated by a porous partition from a normal solution of zinc sulfate. A zinc rod is placed in the zinc sulfate solution and a copper plate in the copper sulfate solution; the current flows through the wire from the copper to the zinc and through the solution from the zinc to the copper.

In the case of metals, *electrolytic solution tension* and *oxidation potential* refer to the same property.

Nernst, who was the first to suggest the above explanation of the origin of the electromotive force on the basis of the relations of osmotic pressure, has worked out a formula for computing the potential difference which exists at the place of contact of a metal with a solution of its ions. If E denotes this potential in volts, R the gas constant expressed in volts $\times$ coulombs,* F the electrochemical equivalent or quantity of electricity borne by one equivalent weight in grams of the ions of any metal, n the valence of the ions, P the electrolytic solution pressure, p the osmotic pressure, and T the absolute temperature of the solution,

* Joules or watt-seconds.

the Nernst formula reads:

$$E = \frac{RT}{nF} \log_e \frac{p}{P}$$

Substituting the numerical values for R (8.32) and F (96,500), dividing by 0.434 in order to use common logarithms, and assuming the ordinary room temperature to be 25° C (= 298° absolute), the formula becomes:

$$E_{25°} = \frac{0.059}{n} \log \frac{p}{P} \text{ volts}$$

Since in dilute solutions the osmotic pressure is proportional to the concentration, c, of the solution, the value c can be used in the equation instead of p, and similarly the concentration C (hypothetical in many cases) which is equivalent to the electrolytic solution pressure can be substituted for P, and the formula for the electrode reaction

$$M \rightleftarrows M^n + n\,e$$

becomes

$$E_{25°} = \frac{0.059}{n} \log \frac{c}{C}$$

Since the logarithm of a fraction is the logarithm of the numerator minus the logarithm of the denominator, the equation can be written

$$E_{25°} = \frac{0.059}{n} (\log c - \log C)$$

$$= -0.059 \log C + 0.059 \log c$$

In this equation, the value C is a constant and is a measure of the inherent oxidation potential of the metal although it cannot be measured directly. If, however, the concentration c is one mole per liter, then, since the log of 1 = 0, the second term in this last equation disappears and we have

$$E_{25°} = -0.059 \log C = E_0 \text{ at } 25°$$

These are the values which are given in tables of normal potentials. To find the value of $E_{25°}$ at any other concentration of the ion involved, we have the equation

$$E_{25°} = E_0 + 0.059 \log c$$

The following table shows the normal potentials of twenty metals and four non-metals; a more complete table is shown on page 46.

NORMAL POTENTIALS

Electrode Reaction	E_0 (volts)	Electrode Reaction	E_0 (volts)
$Li \rightarrow Li^+ + e$	−3.03	$\frac{1}{2} H_2 \rightarrow H^+ + e$	0.00
$K \rightarrow K^+ + e$	−2.93		
$Na \rightarrow Na^+ + e$	−2.72	$Bi \rightarrow Bi^{+++} + 3e$	+0.2
$Ba \rightarrow Ba^{++} + 2e$	−2.8	$Sb \rightarrow Sb^{+++} + 3e$	+0.2
$Mg \rightarrow Mg^{++} + 2e$	−1.5	$As \rightarrow As^{+++} + 3e$	+0.29
$Zn \rightarrow Zn^{++} + 2e$	−0.76	$Cu \rightarrow Cu^{++} + 2e$	+0.34
$S^{--} \rightarrow S + 2e$	−0.55	$I^- \rightarrow \frac{1}{2} I_2 + e$	+0.58
$Fe \rightarrow Fe^{++} + 2e$	−0.43	$2\,Hg \rightarrow Hg_2^{++} + 2e$	+0.80
$Cd \rightarrow Cd^{++} + 2e$	−0.40	$Ag \rightarrow Ag^+ + e$	+0.80
$Co \rightarrow Co^{++} + 2e$	−0.23	$Br^- \rightarrow \frac{1}{2} Br_2 + e$	+1.10
$Ni \rightarrow Ni^{++} + 2e$	−0.22	$\frac{1}{2} O_2 + 2\,H^+ + 2e \rightarrow H_2O$	+1.23
$Sn \rightarrow Sn^{++} + 2e$	−0.14	$Cl^- \rightarrow \frac{1}{2} Cl_2 + e$	+1.36
$Pb \rightarrow Pb^{++} + 2e$	−0.13	$Au \rightarrow Au^+ + e$	+1.5

The theory of oxidation and reduction is based upon these normal electrode potentials. The stronger reducing agents are at the top of the table and the stronger oxidizing agents are at the bottom. If a piece of zinc (normal potential −0.76 volt) is placed in a solution of copper sulfate (normal potential of Cu = +0.34 volt), zinc will go into solution and form Zn^{++} ions while Cu^{++} ions will be reduced and form copper metal. In other words, the zinc has reduced the cupric ions to metal and the zinc has been oxidized by cupric ions. The zinc reaction has taken place in the direction

$$Zn \rightarrow Zn^{++} + 2e$$

and the copper reaction in the direction

$$Cu^{++} + 2e \rightarrow Cu$$

The Daniell cell is based upon these reactions. When the zinc and copper terminals are connected by a wire, there will be a flow of electrons in the electrolyte from the copper to the zinc and in the wire from the zinc to the copper. It is conventional to designate the direction of the electric current by an arrow showing the positive-to-negative direction which is exactly opposite to the direction in which the electrons flow. In the Daniell cell, therefore, the copper is positive to the zinc in the wire. Disregarding small potential drops due to the resistance of the solutions and of the wire, the E.M.F. of the cell when the copper sulfate and zinc sulfate solutions are both molar will be the difference between the normal potential of zinc (−0.76 volt) and the normal potential of copper (+0.34 volt) or 1.1 volts. As the Daniell cell is used, the concentration of the Zn^{++} increases; thus the oxidation potential of the zinc and the concentration of the Cu^{++} increases, raising the oxidation potential of the copper. The Nernst equation

$$E_{25^\circ} = E_0 + \frac{0.059}{n} \log c$$

shows that the oxidation potential of each metal will be −0.21 (half way between −0.76 and +0.34) when the Zn^{++} concentration reaches 7.9×10^{18} moles per liter and the Cu^{++} concentration is only 5×10^{-18} mole per liter. Water will dissolve

only about 5 moles of $ZnSO_4$ per liter, and the quantity $7.9 \times 63.6 \times 10^{-18}$ represents an infinitesimal concentration of copper ions so that we may say that metallic zinc will precipitate copper completely from its solutions. In fact, such a displacement of bivalent ions can take place practically completely if the normal potentials of the two metals are 0.6 volt apart.

From the table of normal potentials, we would expect zinc ($E_0 = -0.76$) to precipitate tin ($E_0 = -0.14$), and this is the case if the solution is neutral. If the solution also contains H^+ ($E_0 = 0.00$), zinc will not precipitate tin from its molar solution, but will liberate hydrogen gas until the potential of hydrogen becomes equal to that of tin

$$E_{25^\circ} = -0.14 = 0.00 + 0.059 \log c \text{ (for hydrogen)}$$

$$\log c = -\frac{0.14}{0.059} = -2.4$$

$$c = 4 \times 10^{-3} \text{ or } p_H = 2.4$$

We are now able to understand why the alkali metals decompose water to form alkali ions and why the quantity of zinc ions formed under similar conditions is very small. The oxidation potential of zinc against a molar solution of zinc ions is about -0.76 volt. Water, however, is ionized very slightly; the table on page 17 gives its ionization product as 1×10^{-14} at 25°. The oxidation potential of hydrogen against such a very dilute solution of hydrogen ions is not 0.0, as given in the table, but it is nearer the zinc value. If the ionization product of water were 10^{-26}, the value would be approximately that of zinc. According to the oxidation potentials, therefore, we should expect zinc to decompose water with liberation of gaseous hydrogen. As a matter of fact, zinc is oxidized somewhat by contact with water and the oxidizing agent is the hydrogen of water; but the reaction does not take place to any appreciable extent. The primary products of the reaction are zinc ions and free hydrogen, but the escape of the hydrogen leaves free hydroxide in solution and this is in equilibrium with the zinc ions. The table on page 23 gives the solubility product of zinc hydroxide as 1.0×10^{-13}. The reason the zinc does not decompose water, therefore, is that it is protected by the film of insoluble oxide or hydroxide which quickly forms upon it. On the other hand, when the hydrogen is present in the form of an acid, with the anion of which zinc forms a fairly soluble salt, the oxidation of the zinc ordinarily continues at the expense of hydrogen ions until all the zinc is dissolved.*

The table also gives valuable information concerning the deposition of metals by electrolysis. The lower the metal is in the potential series the easier it is to deposit it upon the cathode by electrolysis. The table shows the potential which must be overcome to cause electrolytic deposition; by regulating the cathode potential it is possible to accomplish electrolytic separations. The table shows that from molar

* There is another important reason why zinc does not react with water. Hydrogen ions are discharged with different degrees of readiness by electrolysis when cathodes of different metals are used. It is easiest to discharge hydrogen when an electrode of unpolished platinum is used and more voltage is required with zinc and other metals. This so-called *over-voltage* is large enough in the case of zinc to permit the quantitative deposition of this metal by electrolysis of solutions containing acetic acid and sodium acetate. The values given on page 43 are based on the normal discharge of hydrogen, and if the over-voltage of hydrogen toward zinc is considered, it brings the oxidation potential of hydrogen higher in the series.

solutions 0.34 volt more is required to form hydrogen gas than to deposit copper. Therefore, copper is deposited from Cu^{++} solutions before H_2 gas is evolved. By application of the Nernst formula we can compute the concentrations of H^+ and of Cu^{++} when it will be equally easy to deposit copper or liberate hydrogen gas. For copper the Nernst formula gives

$$(1)\ E_{25^\circ} = 0.34 + \frac{0.059}{2} \log c$$

Let us assume that is is desired to deposit copper from 100 ml of a solution which is 1.5 molar in H^+ when all copper has been deposited and that quantities less than 0.1 mg can be neglected. Will it then be possible to deposit all the copper before hydrogen is evolved? If the solution is kept stirred so that copper ions are always available at the cathode, H^+ ions will not be discharged until the potential is equal to that of the Cu^{++} remaining in the solution.

The potential of hydrogen is

$$E_{25^\circ} = 0.00 + 0.059 \log c$$

When $c = 1.5$, $\log c = 0.176$ and $E_{25^\circ} = 0.176 \times 0.059 = 0.010$ for hydrogen in 1.5 molal solution of H^+. Placing this value for E_{25° in equation (1) we get for copper

$$0.0105 = 0.34 + 0.0295 \log c$$

$$\log c = \frac{-0.330}{0.0295} = -11.2 = \overline{12}.8$$

$$c = 6.3 \times 10^{-12}$$

This shows that the concentration of Cu^{++} is reduced to

$$\frac{63.6 \times 6.3 \times 10^{-12}}{10} = 4.0 \times 10^{-8} \text{ mg in 100 ml}$$

before it is equally easy to discharge H^+ from 1.5 molal solution: in other words, a negligible quantity of Cu^{++} remains in solution.

The Nernst equation applies to any reversible oxidation-reduction reaction which can be made to take place at an electrode. The general equation can be written

$$Ox + ne \rightleftarrows Red$$

in which *Ox* represents the oxidizing ion and *Red* is the reducing ion. The general expression for the Nernst equation is then

$$E_{25^\circ} = E_0 + \frac{0.059}{n} \log \frac{[Ox]}{[Red]}$$

and in determining E_0 both of the concentrations must be molar. This means that in applying the Nernst equation we now have to take the concentrations of both the oxidized and reduced ions into consideration, which was not necessary in the case of metals because the concentration of the metal as such in the solution was 0 and did not depend upon the quantity of metal present. In the case of an electrode reaction such as

$$Cr_2O_7^{--} + 6\,e + 14\,H^+ \rightleftarrows 2\,Cr^{+++} + 7\,H_2O$$

the progress of the reaction is also influenced by the concentration of H^+, and its concentration must be molar in determining the E_0 value. The table of normal electrode potentials can be expanded so that it will include every reaction of oxidation and reduction. In the values given in the table, it is assumed that every concentration involved is molar.

The above reaction is not as easily reversible as that of

$$H_3AsO_4 + 2\,H^+ + 2\,e \rightleftarrows H_3AsO_3 + H_2O$$

which can be made to take place quantitatively in either direction by merely regulating the concentration of H^+. The normal oxidation potential for this electrode reaction is 0.57 volt.

For any other concentrations, the Nernst equation is

$$E_{25^\circ} = 0.57 + \frac{0.059}{2}\log\frac{[H_3AsO_4]\,[H^+]^2}{[H_3AsO_3]}$$

This last equation can be written

$$E_{25^\circ} = 0.57 + \frac{0.059}{2}\log\frac{[H_3AsO_4]}{[H_3AsO_3]} + \frac{0.059}{2}\log\,[H]^2$$

and in this form can be used to calculate the effect of changes in $[H^+]$ at a definite $[H_3AsO_4]$ to $[H_3AsO_3]$ ratio.

TABLE OF OXIDATION POTENTIALS

In all the reactions indicated, substances soluble in water are supposed to be present to the extent of 1 mole per liter. Thus the potential given for Li at the top of the table is that of metallic lithium against a molar solution of lithium ions. For the potential $Fe^{++} \rightarrow Fe^{+++}$ it is assumed that both Fe^{++} and Fe^{+++} are present in molar solutions. The potentials are referred to that of hydrogen gas against an electrode of platinum black. In building up a cell from two elements in this table, that element will be positive which lies below the other element in this table. Heavy type signifies a solid. If the signs are reversed the table becomes one of Reduction Potentials.

Reaction	E_0 (volts)	Reaction	E_0 (volts)
$\mathbf{Li} \rightleftarrows Li^+ + e$	−3.03	$\mathbf{Co} \rightleftarrows Co^{++} + 2\,e$	−0.23
$\mathbf{K} \rightleftarrows K^+ + e$	−2.93	$\mathbf{Ni} \rightleftarrows Ni^{++} + 2\,e$	−0.22
$\mathbf{Na} \rightleftarrows Na^+ + e$	−2.72	$V^{++} \rightleftarrows V^{+++} + e$	−0.2
$\mathbf{Ba} \rightleftarrows Ba^{++} + 2\,e$	−2.8	$\mathbf{Cu} + I^- \rightleftarrows \mathbf{CuI} + e$	−0.17
$\mathbf{Sr} \rightleftarrows Sr^{++} + 2\,e$	−2.7	$\mathbf{Ag} + I^- \rightleftarrows \mathbf{AgI} + e$	−0.14
$\mathbf{Ca} \rightleftarrows Ca^{++} + 2\,e$	−2.6	$\mathbf{Sn} \rightleftarrows Sn^{++} + 2\,e$	−0.14
$\mathbf{Mg} \rightleftarrows Mg^{++} + 2\,e$	−1.5	$\mathbf{Pb} \rightleftarrows Pb^{++} + 2\,e$	−0.12
$\mathbf{Al} \rightleftarrows Al^{+++} + 3\,e$	−1.3	$Cr^{++} \rightleftarrows Cr^{+++} + e$	−0.04
$\mathbf{Mn} \rightleftarrows Mn^{++} + 2\,e$	−1.1	$\mathbf{Fe} \rightleftarrows Fe^{+++} + 3\,e$	−0.04
$\mathbf{Zn} \rightleftarrows Zn^{++} + 2\,e$	−0.76	$Ti^{+++} \rightleftarrows Ti^{++++} + e$	−0.04
$\mathbf{Cr} \rightleftarrows Cr^{++} + 2\,e$	−0.6	$H_2\,\text{gas} \rightleftarrows 2\,H^+ + 2\,e$	±0.00
$S^{--} \rightleftarrows \mathbf{S} + 2\,e$	−0.55	$\mathbf{Sn} \rightleftarrows Sn^{++++} + 4\,e$	+0.03
$HS^- + OH^- \rightleftarrows \mathbf{S} + H_2O + 2\,e$	−0.51	$2\,S_2O_3^{--} \rightleftarrows S_4O_6^{--} + 4\,e$	+0.13?
$\mathbf{Ag} + 2\,CN^- \rightleftarrows Ag(CN)_2^- + e$	−0.51	$\mathbf{Sb} \rightleftarrows Sb^{+++} + 3\,e$	+0.2
$\mathbf{Fe} \rightleftarrows Fe^{++} + 2\,e$	−0.43	$Cu^+ \rightleftarrows Cu^{++} + e$	+0.17
$\mathbf{Cd} \rightleftarrows Cd^{++} + 2\,e$	−0.40	$Sn^{++} \rightleftarrows Sn^{++++} + 2\,e$	+0.20
$2\,\mathbf{Cu} + 2\,OH^- \rightleftarrows \mathbf{Cu_2O} + H_2O + 2\,e$	−0.35	$\mathbf{Bi} \rightleftarrows Bi^{+++} + 3\,e$	+0.20
$\mathbf{Pb} + SO_4^{--} \rightleftarrows \mathbf{PbSO_4} + 2\,e$	−0.34	$I_2 + 12\,OH^- \rightleftarrows 2\,IO_3^- + 6\,H_2O + 10\,e$	+0.21
$\mathbf{Tl} \rightleftarrows Tl^+ + e$	−0.33	$\mathbf{Ag} + Cl^- \rightleftarrows \mathbf{AgCl} + e$	+0.23

TABLE OF OXIDATION POTENTIALS — *Continued*

Reaction	E_0 (volts)	Reaction	E_0 (volts)
$Hg_2Cl_2 + 2\,Cl^- \rightleftarrows 2\,HgCl_2 + 2\,e$	+0.24	$\frac{1}{2}\,I_2 + 3\,H_2O \rightleftarrows IO_3^- + 6\,H^+ + 5\,e$	+1.19
$I^- + 6\,OH^- \rightleftarrows IO_3^- + 3\,H_2O + 6\,e$	+0.26	$Au^+ \rightleftarrows Au^{+++} + 2\,e$	+1.2
$2\,Hg + 2\,Cl^- \rightleftarrows Hg_2Cl_2 + 2\,e$	+0.27	$VO^{++} + 3\,H_2O \rightleftarrows VO_4^{---} + 6\,H^+ + e$	+1.2
$As \rightleftarrows As^{+++} + 3\,e$	+0.29	$Tl^+ \rightleftarrows Tl^{+++} + 2\,e$	+1.21
$Cu \rightleftarrows Cu^{++} + 2\,e$	+0.34	$2\,H_2O \rightleftarrows O_2 + 4\,H^+ + 4\,e$	+1.23
$2\,Ag + 2\,OH^- \rightleftarrows Ag_2O + H_2O + 2\,e$	+0.35	$Tl^+ \rightleftarrows Tl^{+++} + 2\,e$	+1.24
$V^{+++} + H_2O \rightleftarrows VO^{++} + 2\,H^+ + e$	+0.4	$Au \rightleftarrows Au^{+++} + 3\,e$	+1.3
$4\,OH^- \rightleftarrows O_2 + 2\,H_2O + 4\,e$	+0.41	$2\,Cr^{+++} + 7\,H_2O \rightleftarrows Cr_2O_7^{--} + 14\,H^+ + 6\,e$	+1.3
$Co \rightleftarrows Co^{+++} + 3\,e$	+0.42	$Mn^{++} + 2\,H_2O \rightleftarrows MnO_2 + 4\,H^+ + 2\,e$	+1.35
$Fe(CN)_6^{----} \rightleftarrows Fe(CN)_6^{---} + e$	+0.44	$\frac{1}{2}\,Cl_2$ gas $\rightleftarrows Cl^- + e$	+1.36
$\frac{1}{2}\,Br_2^0$ liq. $+ 6\,OH^- \rightleftarrows BrO_3^- + 3\,H_2O + 5\,e$	+0.51	$Pb^{++} + 2\,H_2O \rightleftarrows PbO_2 + 4\,H^+ + 2\,e$	+1.44
$Cu \rightleftarrows Cu^+ + e$	+0.51	$Cl^- + 3\,H_2O \rightleftarrows ClO_3^- + 6\,H^+ + 6\,e$	+1.44
$MnO_2 + 4\,OH^- \rightleftarrows MnO_4^- + 2\,H_2O + 3\,e$	+0.52	$Ce^{+++} \rightleftarrows Ce^{++++} + e$	+1.45
$I^- \rightleftarrows \frac{1}{2}\,I_2 + e$	+0.58	$\frac{1}{2}\,Br_2 + 3\,H_2O \rightleftarrows BrO_3^- + 6\,H^+ + 5\,e$	+1.45
$H_3AsO_3 + H_2O \rightleftarrows H_3AsO_4 + 2\,H^+ + 2\,e$	+0.58	$Br^- + 3\,H_2O \rightleftarrows BrO_3^- + 6\,H^+ + 6\,e$	+1.48?
$Br^- + 6\,OH^- \rightleftarrows BrO_3 + 3\,H_2O + 5\,e$	+0.60	$Au \rightleftarrows Au^+ + e$	+1.5
$Tl \rightleftarrows Tl^{+++} + 3\,e$	+0.72	$Cl^- + H_2O \rightleftarrows HClO + H^+ + 2\,e$	+1.51
$Fe^{++} \rightleftarrows Fe^{+++} + e$	+0.75	$Mn^{++} + 4\,H_2O \rightleftarrows MnO_4^- + 8\,H^+ + 3\,e$	+1.52
$Ag \rightleftarrows Ag^+ + e$	+0.80	$MnO_2 + 4\,H_2O \rightleftarrows MnO_4^- + 4\,H^+ + 3\,e$	+1.63
$Hg \rightleftarrows \frac{1}{2}\,(Hg_2)^{++} + e$	+0.80	$2\,H_2O \rightleftarrows H_2O_2 + 2\,H^+ + 2\,e$	+1.66
$H_2O_2 \rightleftarrows O_2 + 2\,H^+ + 2\,e$	+0.85	$\frac{1}{2}\,Cl_2$ gas $+ H_2O \rightleftarrows HClO + H^+ + e$	+1.67
Cl_2 gas $+ 2\,OH^- \rightleftarrows 2\,HClO + 2\,e$	+0.86	$Co^{++} \rightleftarrows Co^{+++} + e$	+1.8
$Hg \rightleftarrows Hg^{++} + 2\,e$	+0 92*		
$Hg_2^{++} \rightleftarrows 2\,Hg^{++} + 2\,e$	+0.95		
NO gas $+ 2\,H_2O \rightleftarrows NO_3^- + 4\,H^+ + 3\,e$	+1.0		
$I^- + 3\,H_2O \rightleftarrows IO_3^- + 6\,H^+ + 6\,e$	+1.02?	$O_2(g) + H_2O(l) \rightleftarrows O_3(g) + 2\,H^+ + 2\,e$	+2.07
$2\,OH^- \rightleftarrows H_2O_2 + 2\,e$	+1.08	$2\,F^- \rightleftarrows F_2(g) + 2\,e$	+2.88
$Br^- \rightleftarrows \frac{1}{2}\,Br_2$ liq. $+ e$	+1.10		

According to the above table, tin and lead occupy neighboring positions with

* The values of the actual potentials of the two mercury combinations given in the table are −0.27 and −0.63 respectively in the presence of normal Cl^- owing to the very slight solubility of Hg_2Cl_2 and the slight ionization of $HgCl_2$.

respect to the oxidation from the metallic to bivalent state. In neutral solutions, either metal will cause an incomplete reduction of the bivalent cations of the other, the reaction stopping when the concentration of stannous ions exceeds sufficiently that of the lead ions, and in the presence of acid no precipitation of tin or lead takes place because it is easier to reduce hydrogen ions than either lead or tin cations, as is shown by the table. On the other hand, the reduction of stannic tin to the stannous condition is shown by the table to be easier than the reduction of hydrogen ions. Consequently in qualitative analysis, lead can be used to reduce an acid solution of a stannic salt without causing any deposition of metallic tin. Antimony is used for the same purpose although the table does not show this quite as clearly because the degrees of ionization and extent of complex formation are not sufficiently known with respect to antimony and tin salts.

Most reactions of oxidation and reduction represent reversible reactions. The strong reducing agents on being oxidized become weak oxidizing agents, and conversely the strong oxidizing agents on being reduced become weak reducing agents. Ordinarily hydrogen is considered a reducing agent, but when a metal replaces the hydrogen of an acid, hydrogen ions act as the oxidizing agent.

The statement that reactions of oxidation and reduction are reversible does not hold rigorously. In the reaction

$$Mn^{++} + 4\ H_2O \rightleftarrows MnO_4^- + 8\ H^+ + 5\ e$$

the Nernst equation for the oxidation potential,

$$E_{25^\circ} = E_0 + \frac{0.059}{5} \log \frac{[H^+]^8\ [MnO_4^-]}{[Mn^{++}]}$$

is not accurate. This is probably due to the tendency to form compounds of manganese having an intermediate valence. Although the effect of H^+ is not as great as this last equation would indicate, it is true that the concentration of H^+ does have an enormous effect upon the oxidation potential. At $p_H = 6$ the oxidation potential of molar MnO_4^- is about 0.6 volt lower than when $p_H = 0$ (normal in H^+). This fact can be used for the fractional oxidation of halides. At $p_H = 5-6$, iodide ion is oxidized to I_2 and bromide or chloride is not oxidized. At $p_H = 3$ bromide is oxidized but chloride is unattacked. The reaction $VO^{++} + 2\ H_2O \rightarrow VO_3^- + 4\ H^+ + e$ is strictly reversible. The Nernst equation is

$$E_{25^\circ} = E_0 + 0.059 \log \frac{[VO_3^-]\ [H^+]^4}{[VO^{++}]}$$

If $[VO_3^-] = [VO^{++}]$, the electrode potential is $+0.92$ when $H^+ = 1$ and 0.68 at $p_H = 1$.

When an element is capable of being oxidized to different degrees, it is possible to compute the reduction potential of a given stage provided the others are known. Thus if we know the reduction potential of **Fe** to Fe^{++} and of Fe^{++} to Fe^{+++}, we can compute what that of **Fe** to Fe^{+++} will be. In fact, if any two of these three potentials are known, the third can be computed. The work required for complete oxidation is the same, whether the complete oxidation takes place all at once or in stages. Electrical work is measured by the quantity of electricity (coulombs) multiplied by the voltage involved. Thus if we represent by a the voltage for **Fe** to Fe^{++}, by b that of Fe^{++} to Fe^{+++}, and by c that of **Fe** to Fe^{+++}, and use the symbol F to represent a faraday, or 96,500 coulombs of electricity, then for the oxidation of 55.84 g of iron we have $2\ F \cdot a + F \cdot b = 3\ F \cdot c$; or $2\ a + b = 3\ c$.

We have already seen (p. 19) that the solubility of a slightly soluble salt A_mB_n can be expressed by its solubility product $[A]^m \cdot [B]^n$. If another substance is present yielding either A or B ions, then less of the other ion is required from the difficultly soluble substance in order to reach the solubility product. The substance, therefore, is less soluble in a solution containing a common ion than it is in pure water. The application of this principle to salts which are very soluble in water is seldom helpful. Sodium chloride, for example, is much less soluble in strong hydrochloric acid solutions than would be predicted.

The relations are quite different when one of the original substances is difficultly soluble or only slightly ionized. Thus when a precipitate of silver chloride is formed, the solution is saturated with the salt and the solubility product of the ions has been reached. If now a small amount of either chloride or silver ions is added to the saturated solution of silver chloride, further precipitation of silver chloride should take place. In general, therefore, a slight excess of precipitant will make a precipitate less soluble. There are exceptions to this rule, however. The rule does not hold if one of the ions from the precipitate shows a tendency to form a soluble complex ion with the excess of precipitant. Thus silver chloride is, in fact, less soluble in very dilute sodium chloride solution than it is in water, but it dissolves in a saturated brine solution more than in pure water, owing to the formation of a complex ion. Barium sulfate is less soluble in dilute sulfuric acid than it is in water, but concentrated sulfuric acid dissolves it quite readily. In this case, probably HSO_4^- is formed, but it should also be noted that the solvent is now concentrated sulfuric acid and not water. Aluminum hydroxide is precipitated by the very careful neutralization of a solution containing an aluminum salt, but the hydroxide dissolves in sodium hydroxide solution, forming sodium aluminate. None of these examples is contrary to the mass-action law, but each shows the need of considering all the possible reactions.

When a weak electrolyte is present in solution, the effect of the common ion is often quite remarkable. A weak acid such as acetic acid is ionized much less in a solution containing alkali acetate than it is in pure water, hydrochloric acid greatly represses the ionization of hydrogen sulfide, and ammonium salt weakens the basicity of ammonia solutions to a marked degree. In an aqueous solution of a weak acid, HA, the extent of the ionization is indicated by the magnitude of its ionization constant

$$\frac{[H^+][A^-]}{[HA]} = K_a$$

and we can say

$$[H^+] = \frac{[HA]}{[A^-]} K_a \qquad (1)$$

If we turn to the table of ionization constants on page 16, we shall find that the values are given to only two significant figures. In computations involving these constants, therefore, it is a waste of time to attempt to define, with great precision, quantities involved. In a solution of acetic acid and sodium acetate, the hydrogen ions come from the acetic acid and from water but the ionization of water is so slight that no serious error is introduced if we assume that all the H^+ comes from the acetic acid. The acetate ions come from the sodium acetate and from the acetic acid, but when at least an equivalent quantity of the salt has been added we can assume the acetate-ion concentration to be that of the salt added. If we call the concentration of the weak acid c_a and that of the salt c_s (both expressed in moles per liter), equation (1) above becomes

$$[H^+] = \frac{c_a}{c_s} K_a \tag{2}$$

This is only an approximate expression. Somewhat greater accuracy can be obtained by calling $[HA] = c_a - [H^+]$ and $[A^-] = c_s + [H^+]$ because the acid yields an equal quantity of H^+ and A^- ions. Equation (2) then becomes

$$[H^+] = \frac{(c_a - [H^+])}{C_s + [H^+]} K_a \tag{3}$$

This gives a quadratic which is easy to solve when the numerical values of K_a, c_a and c_s are inserted. Then for c_s instead of the moles of salt per liter the *activity* should be used where the greatest possible accuracy is desired.

When the value of $[H^+]$ is computed for 0.1 N acetic acid in the presence of 0.1 N sodium acetate by formula (2) above, the result is 0.0000174, and when computed more carefully as just indicated the value is practically the same, which shows that the approximation formula gives results which are sufficiently accurate for most purposes.

In a solution of a weak base, BOH which ionizes to a slight extent into B^+ and OH^- ions and has the ionization constant

$$\frac{[B^+]\ [OH^-]}{[BA]} = K_b$$

the same reasoning shows that an approximation of the OH^- concentration in a solution containing the weak base and one of its soluble salts is

$$[OH^-] = \frac{[BOH]}{[B^+]} K_b = \frac{c_b\ K_b}{c_s}$$

and since

$$[H^+] = \frac{K_w}{[OH^-]} \text{ (cf. p. 17)}$$

we have

$$[H^+] = \frac{K_w c_s}{K_b c_b}$$

where c_s is the concentration of the salt of the weak base and c_b is the concentration of the weak base itself.

Solutions containing a weak acid and its salt or a weak base and its salt are called *buffer solutions*. They resist a change in hydrogen-ion concentration when a small quantity of acid or base is added. Thus a solution which is 0.1 *N* in acetic acid and 0.1 *N* in sodium acetate has $p_H = 4.75$. If to 100 ml of this solution there is added 1 ml of 0.1 *N* sodium hydroxide, the mixture then has $p_H = 4.755$. In analytical chemistry much use is made of these buffer solutions.

The effect of hydrogen ions upon the ionization of hydrogen sulfide is similar. The solubility product of copper sulfide is 8.5×10^{-45} and that of zinc sulfide is 1.2×10^{-23}. The precipitation of both copper and zinc by hydrogen sulfide is practically complete in a solution containing no excess hydrogen ions. As the metal precipitates, however, hydrogen ions are formed:

$$Zn^{++} + H_2S \rightarrow ZnS + 2\,H^+$$

The accumulation of these hydrogen ions serves to repress the ionization of hydrogen sulfide and tends to stop the precipitation of the zinc. If, therefore, we wish to precipitate copper and have zinc in solution, all that is necessary is to add a little acid at the start; in 0.3 *N* acid solution the precipitation of the copper as sulfide is practically complete, while little if any zinc sulfide is precipitated. On the other hand, if some sodium acetate is added to the solution, slightly ionized acetic acid is formed and the accumulation of the hydrogen ions is prevented. This effect is so great that it is easier to precipitate zinc sulfide from a solution containing acetic acid and sodium acetate than from a solution of zinc chloride in water. The concentration of hydrogen ions is kept very low, even though the solution may smell strongly of non-ionized acetic acid.

The common-ion effect is also involved in the dissolving of precipitates. The effect is shown, for example, when calcium phosphate is dissolved by acid. The table on page 11 shows that the tertiary ionization of phosphoric acid is about the same as the secondary ionization of hydrogen sulfide and the secondary ionization is comparable to the primary ionization of hydrogen sulfide. If many hydrogen ions are added in the form of a mineral acid, the ionization of HPO_4^{--} and of $H_2PO_4^-$ becomes extremely small. The saturated solution of calcium phosphate contains Ca^{++} and PO_4^{---} ions. These PO_4^{---} ions must be in equilibrium with added hydrogen ions. When the PO_4^{---} from HPO_4^{--} is kept less than the PO_4^{---} concentration corresponding to the value of a saturated solution of calcium phosphate,

the calcium phosphate must tend to dissolve. As $Ca(H_2PO_4)_2$ is much more soluble than $CaHPO_4$, which in turn is more soluble than $Ca_3(PO_4)_2$, it is desirable to add enough acid to make the $H_2PO_4^-$ practically non-ionized.

The common-ion effect which is involved in nearly every reaction of precipitation and of dissolution represents an application of the mass-action principle.

Hydrolysis

The reaction between an acid HA and a base BOH can be expressed

$$HA + BOH \rightleftarrows H_2O + BA \qquad (1)$$

If this reaction takes place in the direction left to right it is called *neutralization;* the reverse reaction is called *hydrolysis.*

If the acid and base as well as the salt are ionized practically completely, the anion of the acid and the cation of the base do not take part in the reaction and the neutralization reaction is really

$$H^+ + OH^- \rightarrow H_2O \qquad (2)$$

The reaction between a strong base and a strong acid will take place practically completely and the H^+ and OH^- concentrations at the end will correspond to the ionization of water (see p. 17). The salts of strong acids and bases are not hydrolyzed appreciably.

If the acid, the base, or both are only slightly ionized, equation (2) does not properly express reaction (1). If the acid is weak and the base strong, the reaction becomes

$$HA + OH^- \rightleftarrows H_2O + A^- \qquad (3)$$

If the acid is strong and the base is weak, we have

$$H^+ + BOH \rightleftarrows H_2O + B^+ \qquad (4)$$

If both acid and base are weak, the reaction is

$$HA + BOH \rightleftarrows H_2O + B^+ + A^- \qquad (5)$$

These last three neutralizations do not take place as completely as does the reaction between a strong acid and a strong base and the reverse reaction of hydrolysis becomes appreciable.

I. Hydrolysis of Salts of Weak Acids and Strong Bases

The base formed by the hydrolysis is largely ionized, while the acid is only slightly so. Here the reaction is the reverse of equation (3) and the equation of hydrolysis is

$$A^- + H_2O \rightleftarrows HA + OH^- \qquad (6)$$

As a result of the hydrolysis, the aqueous solution of the salt will have a greater OH^- concentration than water has; in other words, the p_H of the aqueous solution of the salt will be greater than 7 (see p. 18). Reaction (6) is reversible and the mass-action law applies to it

$$\frac{[HA]\,[OH^-]}{[A^-]} = K_{hydr.} \tag{7}$$

In this expression it is not necessary to take into consideration the concentration of the water itself, which can be considered constant. The value $K_{hydr.}$ is called the *hydrolysis constant*. It can be shown to be a simple function of K_a, the ionization constant of the acid, and K_w, the ion product of water (10^{-14} at room temperature; cf. p. 17).

If we multiply both numerator and denominator of equation (7) by the concentration of H^+ in the solution, we get

$$\frac{[HA]\,[H^+]\,[OH^-]}{[H^+]\,[A^-]} = K_{hydr.} \tag{8}$$

Then since

$$\frac{[HA]}{[H^+]\,[A^-]} = \frac{1}{K_a} \quad \text{and} \quad [H^+]\,[OH^-] = K_w$$

We have

$$\frac{[HA]\,[OH^-]}{[A^-]} = \frac{K_w}{K_a} = K_{hydr.} \tag{9}$$

Now in equation (6) it is clear that equal quantities of HA and OH^- are formed as a result of the hydrolysis of a salt of a weak acid and a strong base. In equation (9) therefore we can call $[HA] = [OH^-]$ and we can substitute the concentration of the salt c for the value of $[A^-]$. With these approximations we have

$$\frac{[OH]^2}{c} = \frac{K_w}{K_a} \quad \text{and} \quad [OH^-] = \sqrt{\frac{K_w}{K_a}\,c}$$

Since

$$[H^+] = \frac{K_w}{[OH^-]}$$

we have

$$[H^+] = \frac{K_w}{\sqrt{\frac{K_w c}{K_a}}} = \sqrt{\frac{K_a K_w}{c}} \tag{10}$$

Solving this equation with logarithms we get

$$\log [H^+] = \tfrac{1}{2} \log K_a + \tfrac{1}{2} \log K_w - \tfrac{1}{2} \log c$$

or

$$-\log [H^+] = -\tfrac{1}{2} \log K_a - \tfrac{1}{2} \log K_w + \tfrac{1}{2} \log c \tag{11}$$

Now

$$p_H = \log \frac{1}{[H^+]} = -\log [H^+]$$

$$p_a = \log \frac{1}{K_a} = -\log K_a$$

$$p_w = \log \frac{1}{K_w} = -\log K_w = 14$$

Substituting these values in equation (11) we get an expression which tells us the approximate p_H of an aqueous solution of a salt of a weak acid and a strong base.

$$p_H = 7 + \tfrac{1}{2} p_a + \tfrac{1}{2} \log c \qquad (12)$$

Suppose that it is desired to know the approximate p_H of a solution which is 0.025 N in sodium acetate. Since both of the ions of this salt are univalent we can assume that the concentration of the acetate ion and of the salt is 2.5×10^{-2} mole per liter. The logarithm of this value is written $\bar{2}.40$ or $8.40 - 10$. In either case the actual value is -1.60, and $0.025 = 10^{-1.6}$. The value of $\frac{1}{2} \log c$ is, therefore, -0.80. The ionization constant of acetic acid is $0.0000174 = 1.74 \times 10^{-5}$, and $p_a = 4.76$.

Substituting these values in equation (12) we get

$$p_H = 7 + 2.38 - 0.80 = 8.58$$

Owing to the presence of the OH^- ions in appreciable quantity, all salts of this category react alkaline. The alkali salts of hydrocyanic acid, hypochlorous acid, carbonic acid, boric acid, and hydrogen sulfide are of this type.

II. Hydrolysis of Salts of Strong Acids and Weak Bases

Here the conditions are reversed, and it is the acid which is almost completely dissociated and the base but slightly. The hydrolysis in this case is the reverse of equation (4). The mass-action expression for the reaction

$$B^+ + H_2O \rightleftharpoons H^+ + BOH \qquad (13)$$

is

$$\frac{[BOH]\,[H^+]}{[B^+]} = K_{hydr.} \qquad (14)$$

Multiplying both numerator and denominator by $[OH^-]$ we get

$$\frac{[BOH]\,[H^+]\,[OH^-]}{[B^+]\,[OH^-]} = \frac{K_w}{K_b} = K_{hydr.} \qquad (15)$$

Equation (13) shows that there is formed by hydrolysis an equal quantity of H^+ and BOH, and we can disregard the very small quantity of

H^+ from the ionization of water. In equation (14) therefore, we can substitute $[H^+]$ for [BOH], and c, the concentration of the salt, for $[B^+]$. This gives us

$$\frac{[H^+]^2}{c} = \frac{K_w}{K_b} = K_{hydr.} \tag{16}$$

and

$$[H^+] = \sqrt{\frac{K_w c}{K_b}}$$

Solving with logarithms,

$$\log [H^+] = \tfrac{1}{2} \log K_w + \tfrac{1}{2} \log c - \tfrac{1}{2} \log K_b$$

and

$$-\log [H^+] = -\tfrac{1}{2} \log K_w - \tfrac{1}{2} \log c + \tfrac{1}{2} \log K_b \tag{17}$$

Substituting the values $p_H = -\log [H^+]$, $p_w = -\log K_w = 14$, and $p_b = -\log K_b$, we have for an aqueous solution of a salt of a weak base and a strong acid

$$p_H = 7 - \tfrac{1}{2} p_b - \tfrac{1}{2} \log c \tag{18}$$

Salts of this class, such as those of ammonium, chromium, aluminum, iron, etc., react acid when in aqueous solution.

In the case of polyvalent bases hydrolysis takes place in stages:

$$RCl_2^+ + H_2O \rightleftarrows RCl_2OH + H^+$$

$$RCl^{++} + 2\,H_2O \rightleftarrows RCl(OH)_2 + 2\,H^+$$

$$R^{+++} + 3\,H_2O \rightleftarrows R(OH)_3 + 3\,H^+$$

Ferric, aluminum, and chromic chlorides, for example, react acid in aqueous solution. If such solutions are evaporated to dryness, considerable hydrochloric acid is volatilized, and the residue obtained is an insoluble basic salt which can be dissolved only by means of acid. If an aqueous solution of ammonium chloride is boiled, the ammonia formed by hydrolysis evaporates more rapidly than the hydrochloric acid; the distillate is distinctly basic and the undistilled liquid becomes more acid.

III. Hydrolysis of Salts of Weak Acids and Weak Bases

The acids and bases formed by hydrolysis are only slightly dissociated. In this case, the equation of hydrolysis is the reverse of equation (5) and is

$$B^+ + A^- + H_2O \rightleftarrows HA + BOH$$

The mass-action expression is

$$\frac{[HA]\,[BOH]}{[B^+]\,[A^-]} = K_{hydr.} \tag{19}$$

Multiplying both numerator and denominator by $[H^+] \cdot [OH^-]$ and remembering that [HA] = [BOH], we get

$$\frac{[HA]\,[BOH]\,[H^+]\,[OH^-]}{[H^+]\,[A^-]\,[B^+]\,[OH^-]} = \frac{K_w}{K_a \cdot K_b} = K_{hydr.} \tag{20}$$

If we let c = concentration of the salt and assume that $c = [A^-] = [B^+]$ in equation (19) we get with the aid of equation (20)

$$[BOH] = [HA] = c\sqrt{\frac{K_w}{K_a \cdot K_b}} \tag{21}$$

Since

$$\frac{[H^+]\,[A^-]}{[HA]} = K_a, \quad [HA] = \frac{[H^+]\,[A^-]}{K_a}$$

Substituting this value of [HA] in equation (21) and calling $[A^-] = c$, we get

$$[H^+] = \frac{K_a}{c} \cdot c\sqrt{\frac{K_w}{K_a K_b}}$$

$$= \sqrt{\frac{K_a \cdot K_w}{K_b}} \tag{22}$$

Solving with logarithms,

$$\log [H^+] = \tfrac{1}{2} \log K_a + \tfrac{1}{2} \log K_w - \tfrac{1}{2} \log K_b$$

and

$$-\log [H^+] = -\tfrac{1}{2} \log K_a - \tfrac{1}{2} \log K_w + \tfrac{1}{2} \log K_b$$

Substituting the values $p_H = -\log H$, $14 = -\log K_w$, $p_a = -\log K_a$, and $p_b = -\log K_b$, we get $p_H = 7 + \tfrac{1}{2} p_a - \tfrac{1}{2} p_b$ (23)

Notice that $[H^+]$ and p_H do not depend upon the concentration of the salt when all the above assumptions have been made. Equation (23) is only approximately true, however, because we have assumed complete ion activity of the salt and that [BOH] is equal to [HA]. Neither of these assumptions is altogether correct, but the formula gives good approximations when the hydrolysis is less than 5 per cent.

Salts of this type are especially subject to hydrolysis, and, as both the acid and base are slightly ionized, the hydrolysis may take place to a considerable extent without the solution manifesting either acid or basic properties.

If the ionization of the acid is greater than that of the base, the solution reacts acid; and conversely, when the base is stronger than the acid the solution of the salt shows an alkaline reaction.

Neutral ferric acetate in a *boiling*, aqueous solution is hydrolyzed:

$$Fe(C_2H_3O_2)_3 + 2\,H_2O \rightleftarrows Fe(OH)_2C_2H_3O_2 + 2\,HC_2H_3O_2$$

Basic ferric acetate is precipitated and can be removed by filtering the hot solution. If the solution is allowed to cool, the reaction tends to take place in the reverse direction and some of the basic salt goes into solution. *Heat and dilution always favor hydrolysis.**

IV. Hydrolysis of Salts of Strong Acids with Strong Bases

Salts of this type yield, by hydrolysis, acids and bases which are almost entirely dissociated in dilute aqueous solution, and the general equation becomes:

$$K_{hydr.} = \frac{[B^+]\,[OH^-]\,[H^+]\,[A^-]}{[B^+]\,[A^-]} = [H^+]\,[OH^-]$$

The H^+ and OH^- ions, however, are in equilibrium with undissociated water; the solution reacts neutral and contains only as many H^+ and OH^- ions as correspond to the ionization of water, which is so small that there remains only the electrolytic dissociation of the salt to be considered. *Salts of this type are not subject to appreciable hydrolysis.*

The hydrolytic action of water, as well as the mass-action law, may be illustrated by the following experiment: A little water, added to a solution of antimony chloride in concentrated hydrochloric acid, causes precipitation of antimony oxychloride,

$$Sb\begin{matrix}\diagup Cl \\ - Cl \\ \diagdown Cl\end{matrix} + H_2O \rightleftarrows Sb\begin{matrix}\diagup\!\!\!\!\diagup O \\ \diagdown Cl\end{matrix} + 2\,HCl$$

which dissolves on adding a little concentrated hydrochloric acid. Further addition of water again precipitates the basic salt, which will dissolve in more of the concentrated acid, etc. It is obvious that by increasing the mass action of the water the reaction goes from left to right, while by increasing the concentration of the hydrochloric acid it goes from right to left.

The analytical chemist frequently desires to assist or to prevent hydrolysis. The mass-action principle shows how this can be done. To assist a chemical reaction it is necessary to increase the concentration of one of the original reacting substances or to lessen the concentration of one of the substances formed. Aside from the reactions of oxidation and reduction, all the reactions that take place completely in aqueous solution are those in which the concentration of one of the substances formed is practically negligible. This is due to the formation of (1) a precipitate, (2) a gas, or (3) an undissociated substance (cf. p. 29). Neutralization takes place between an acid and a base because of the tendency to form undissociated water. Hydrolysis is the reverse of neutralization and is due to the fact that water is slightly dissociated; it takes place when one of the products is a gas, a precipitate, or an undissociated substance. Thus the hydrolysis of a salt of a weak acid and a strong base is due to the fact that the dissociation of the weak acid is slight. The hydrolysis of a salt of a strong acid and a weak base is due to the formation of the undissociated base. Hydrolysis takes place most readily when both the acid and the base are weak, because then both the H^+ ions and the OH^- ions are removed from the solution to form

* The value of K_w (cf. p. 17) is 1.0×10^{-14} at 25° and 5.1×10^{-13} at 100°. The increased ionization of the water favors hydrolysis.

undissociated acid and undissociated base. Hydrolysis of a salt of a strong acid and a strong base cannot take place because there is then no tendency for the H^+ and OH^- ions of water to be removed. To assist hydrolysis, boiling is advisable, because water is much more dissociated at this temperature than when cold. The reaction that takes place on boiling often proceeds in the other direction on cooling, simply on account of the change in the ionization of the water itself. Dilution favors hydrolysis because it diminishes the concentration of the substances formed; the concentration of the ions from water is not changed, but the relative proportions of these ions to other ions present is increased. Hydrolysis is also favored when one of the products is gaseous or insoluble; thus ammonium carbonate is very easily hydrolyzed, not only because the acid and base are both weak but also because both ammonia and carbon dioxide are volatile; ferric acetate is hydrolyzed not only because the acid and base are both weak, but also because the basic ferric acetate is very insoluble. Finally, to stop hydrolysis it is only necessary to add a little free acid or free base at the start; the efficiency of the acid or base is proportional to the extent to which it is itself ionized. If the solution becomes alkaline as a result of hydrolysis, then a little alkali will best stop hydrolysis, but if the solution becomes acid, a little acid should be added. Moreover, it is advisable to work in cold and concentrated solutions. A dilute aqueous solution of potassium cyanide has the odor of free hydrocyanic acid and reacts alkaline to litmus, but if a little caustic potash is added, the hydrolysis of the salt is prevented and the odor of hydrocyanic acid can be detected no longer. Similarly, boiling a solution of neutral ferric sulfate results in the precipitation of a basic salt, but the precipitation does not take place if a little sulfuric acid is added at the start.

Amphoteric Electrolytes

During the first half of the nineteenth century, oxygen was regarded as an essential constituent of all acids. In the dualistic theory of Berzelius, there were two kinds of oxides — positive oxides which unite with water to form bases, and negative oxides which unite with water to form acids. Salts result from a union of these positive and negative oxides.

The terms positive and negative are relative, and it was recognized that some oxides were positive to certain oxides but negative to others. Thus stannous oxide, SnO, can unite with the more positive sodium oxide, Na_2O, and form the salt sodium stannite, $Na_2O \cdot SnO$, or it can form a sulfate, $SnO \cdot SO_3$, with the more negative sulfur trioxide.

The characteristic of an acid* is that it is capable of furnishing hydrogen ions when dissolved in water; and the characteristic property of a base is the ability to form hydroxide ions in aqueous solutions. The neutralization of an acid by a base is characterized by the uniting of hydrogen ions from an acid with hydroxide ions from a base.

Chemists, however, still regard substances such as ferrous silicate, $FeSiO_3$, as salts, although ferrous oxide and silicon dioxide do not dissolve

* Cf. p. 6.

in water and form hydroxide and hydrogen ions, respectively. Ferrous silicate is regarded as a salt of the hypothetical metasilicic acid, H_2SiO_3, and of the hypothetical ferrous hydroxide, $Fe(OH)_2$. Silicic acid is a hypothetical acid because, although it does not form hydrogen ions when mixed with water, the salt $FeSiO_3$ is what we would expect to form from H_2SiO_3 and $Fe(OH)_2$, although these compounds may not exist or, if they do, they are not appreciably soluble in water and cannot yield ions.

A study of the periodic table of the elements shows that the families on the left side form bases more readily than those on the right side. In any one family, the tendency to form bases rather than acids is more pronounced as the atomic weight of the element increases. With any given element, however, the tendency to form an acid increases as the valence of the element is raised. For example, we find that phosphoric acid is a stronger acid than silicic acid and a weaker acid than sulfuric acid. Silicon, phosphorus, and sulfur follow one another in the periodic table. Phosphoric acid, in which the valence of the phosphorus is five, is a stronger acid than phosphorous acid in which the valence of the phosphorus is three. Antimony, which, like phosphorus, is in Family V, forms acids which are much weaker than the corresponding acids of phosphorus; in bismuth, which is also in Family V, the tendency to form an acid has almost entirely disappeared.

As a general rule, when the positive charge on an element is increased, it becomes more difficult for the corresponding hydroxide to ionize as a base and the tendency for the hydroxide to ionize as an acid increases. Thus the higher the positive charge on the atom, the more *negative* it becomes according to the old-fashioned conception. This apparent contradiction is not quite as inconsistent as it seems; it arises from a confusion of the *intensity* factor of electric energy with the *quantity* factor. All forms of energy are composed of these two factors, and such confusion of the factors is quite common.

The quantity of electricity corresponding to a unit electric charge on a gram atom of any element is 96,500 coulombs. All univalent elements bear this charge, and all bivalent elements twice as much. On the other hand, the tendency of the atoms to accept or give up electrons varies greatly, as the table of oxidation potentials shows (p. 46). The elements which show the greater tendency to give up one or more electrons of negative electricity have been held to be more positive than those which show less tendency to lose electrons. In other words, the elements nearer the top of the electromotive series have been regarded as more positive than those which are below them in this series. Thus the older conception of positive and negative nature was largely one of electromotive force, or voltage, rather than one of electric nature or quantity of electricity. It corresponds to the behavior of the elements in an electric couple such as that of the Daniell cell; the zinc becomes the

anode in such a cell, and the copper the cathode; the electrons flow through the cell from the copper to the zinc and the zinc is positive to the copper *in the solution*. The student should be careful to distinguish in his own mind the difference between the meaning of the word positive when used in this sense of voltage and when used to represent the character of an electric charge.

Water is a substance which ionizes to a slight extent, and the initial products of the ionization are H^+ and OH^-. Water, therefore, may be considered as being both an acid and a base. There are other substances which act as acids without forming at one time any more hydrogen ions than does water and other basic substances which do not form more hydroxide ions. Water is characterized by the fact that it forms an equal amount of both hydrogen and hydroxide ions by its primary ionization. Other hydroxides are known which have both acid and basic properties, but this is due to two distinct kinds of ionization. At one time they dissociate as acids and at another time as bases. Such substances are said to be *amphoteric electrolytes*.

Aluminum hydroxide is an amphoteric electrolyte. This substance has a very small solubility product, and the quantity of ions present in the saturated solution is extremely small. The chemical behavior of aluminum hydroxide shows, however, that it is capable of dissociating in two ways:

$$Al(OH)_3 \rightarrow Al(OH)_2^+ + OH^- \text{ (ionization as a base)}$$

$$Al(OH)_3 \rightarrow H^+ + AlO_3H_2^- \rightarrow H^+ + AlO_2^- + H_2O \text{ (ionization as an acid)}$$

The mass-action principle enables one to predict which of these ionization reactions will take place. In the presence of a strong acid, such as hydrochloric acid, the common-ion effect of the hydrogen ions will prevent the ionization of the aluminum hydroxide as an acid; the effect is much more marked than that of sodium acetate upon acetic acid, for in this case the difference in the percentage ionization of hydrochloric acid and aluminic acid is much greater. On the other hand, the presence of the hydrogen ions favors the ionization of the aluminum hydroxide as a base. To establish the proper equilibrium between H^+, OH^-, and H_2O, nearly all the OH^- ions from the aluminum hydroxide react with the H^+ of the hydrochloric acid. On account of this removal of the OH^-, the ionization of the $Al(OH)_3$ progresses, the $Al(OH)_2^+$ ionizes into $Al(OH)^{++}$ and OH^-, and finally the $Al(OH)^{++}$ ionizes into Al^{+++} and OH^-. In this way $Al(OH)_3$ dissolves to form Al^{+++}.

Similarly, in the presence of sodium hydroxide, the common-ion effect of the OH^- prevents the aluminum hydroxide from ionizing as a base and the H^+ ions formed by its dissociation as an acid react with the

OH^- ions from the sodium hydroxide, and the final result is that all the aluminum dissolves as sodium aluminate, $NaAlO_2$.

Whenever an oxide or hydroxide dissolves by chemical reaction with an acid, and also by chemical reaction with a base, the substance is obviously an amphoteric electrolyte.

Detection of Acids and Bases. Theory of Indicators

To detect the presence of free hydrogen cations or of hydroxide anions, certain colored organic substances are used, called *indicators*. These indicators are very weak acids, very weak bases, or amphoteric substances, and the free acid or base is an unstable substance which tends to undergo a slight rearrangement of the atoms in order to assume a condition of greater stability. The color of any organic compound is due to a certain special arrangement of certain atoms, the *chromophore* group; when this arrangement is changed, the color also is changed or lost.

The concentration of hydrogen ions can also be determined electrometrically by measuring the electromotive force of a hydrogen electrode placed in the solution and connected with an electrode of known electromotive force such as a standard calomel cell. If the electromotive force thus determined is compared with that of a normal hydrogen electrode, the Nernst formula (p. 42) takes the form $E_{25^\circ} = 0 + 0.059 \log c$, in which c is the concentration of hydrogen ions in moles per liter. By potentiometric measurements, therefore, it is possible to determine the hydrogen-ion concentrations at which a given indicator changes color. In neutralization reactions, the hydrogen-ion concentrations are always small when the neutralization is complete, so that it is convenient to use $\log \frac{1}{[H^+]} = p_H$, the hydrogen exponent, rather than the concentration c.

When an acid is neutralized by a base, the resulting aqueous solution of salt at the equivalence point will show $p_H = 7$ only when the acid and base are equally strong with respect to ionization. If the acid is stronger than the base, then the aqueous solution of the salt will show $p_H < 7$; but if the base is stronger than the acid then the aqueous solution of the salt will show $p_H > 7$. Ordinary distilled water usually contains carbonic acid enough to make its p_H = about 5.5.

The indicators most used in qualitative analysis are *methyl orange* which is red or pink in acid solutions and is turned yellow by bases, *phenolphthalein* which is colorless in acid solutions and turns pink when free base is present, and *litmus* which is red with acids and blue with bases. Of these indicators methyl orange is most sensitive to weak

bases and phenolphthalein to weak acids. Indicators are known, however, which change color at p_H values ranging from 1 to nearly 14. In the following table the color in acid solutions is given first and then the color in basic solutions. Under the heading "p_H Range" is given the region where the indicator undergoes a change in color.

To prepare methyl orange solution, dissolve 0.02 g of the solid in 100 ml of hot water, allow to cool, and filter if necessary.

To prepare phenolphthalein solution, dissolve 1 g of the solid in 100 ml of 85 per cent alcohol.

To prepare litmus solution, place the commercial cubes in a porcelain dish, without powdering, cover with 85 per cent alcohol, and digest on the water bath with frequent stirring. Decant off the solution, and repeat these operations three times to remove the undesirable coloring matter. Extract the residue with hot water and allow the extract to settle in a tall cylinder for several days. Siphon off the clear liquid, evaporate it to about one-third its original volume, and make acid with acetic acid to decompose any potassium carbonate present. Evaporate to sirupy consistency on the water bath and cover the mass with considerable 90 per cent alcohol. Filter and dissolve the residue in sufficient hot water so that 3 drops of the solution will be necessary to impart a distinct color to 50 ml of water.

To prepare methyl red solution, dissolve 0.1 g of solid in 300 ml of alcohol and dilute with water to 500 ml.

To prepare cresolphthalein, dissolve 0.1 g of pure *o*-cresolphthalein in 500 ml of 95 per cent alcohol.

To prepare indicator solutions of *thymol blue, bromophenol blue, bromocresol purple, bromothymol blue, phenol red,* and *cresol red,* triturate 0.1 g of the solid with an equivalent quantity of 0.05 *N* sodium hydroxide solution. Dilute with water to 500 ml in the case of the last two of the above indicators and to 250 ml with the other four.

Name of Indicator	Color Change	p_H Range
1. Thymol blue	Red–yellow	1.2–2.8
2. Bromophenol	Yellow–blue	3.0–6.0
3. Methyl orange	Red–yellow	4.0–5.0
4. Methyl red	Red–yellow	4.4–6.0
5. Cochineal	Yellow–lilac	5.0–6.0
6. Bromocresol purple	Yellow–purple	5.2–6.8
7. Litmus	Red–blue	6.0–7.0
8. Bromothymol blue	Yellow–blue	6.0–7.6
9. Phenol red	Yellow–red	6.8–8.4
10. Phenolphthalein	Colorless–red	8.0–9.0
11. Cresol red	Yellow–red	7.2–8.8
12. Thymol blue	Yellow–blue	8.0–9.6
13. Cresolphthalein	Colorless–red	8.2–9.8
14. Thymolphthalein	Colorless–blue	9.0–10.0
15. Tropaeolin 0	Yellow–orange yellow	11–12
16. Trinitrobenzene	Colorless–orange	12–13
17. Benzopurpurin	Yellow–red	13–14

Let HIn represent any indicator acid and InOH any indicator base. For the ionization reactions

$$HIn \rightleftarrows H^+ + In^-$$
$$InOH \rightleftarrows In^+ + OH^-$$

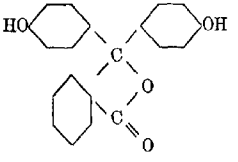
the mass-action expressions are

$$\frac{[H^+]\ [In^-]}{[HIn]} = K_a \quad \text{and} \quad \frac{[In^+]\ [OH^-]}{[InOH]} = K_b$$

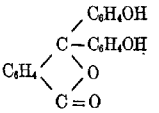
The values K_a and K_b are the ionization constants:

$$\log \frac{1}{K_a} = -\log K_a \quad \text{and} \quad \log \frac{1}{K_b} = -\log K_b$$

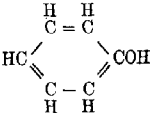
have been termed the *indicator constants*. It is a characteristic of the indicators that, when the free acid or free base is formed, it quickly undergoes a slight change in the arrangement of the atoms in the molecule and as a result of this rearrangement there is a change in color. Thus in the case of phenolphthalein, the colorless acid has the structure



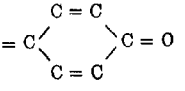
or



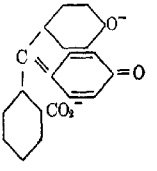
The compound is made from two molecules of phenol, C_6H_5OH, and one molecule of phthallic acid anhydride, $C_6H_4\begin{matrix}CO\\CO\end{matrix}O$. In the colorless form it is believed that in each of the three C_6H_4 rings there are alternate single and double bonds between the six carbon atoms. Thus phenol itself can be written



When the salt is formed, this benzenoid structure is changed to what is called the quinoid structure



The dibasic colored phenolphthalein anion, therefore is



Colloidal Solutions

If an alkaline silicate in dilute solution is mixed with dilute hydrochloric acid, the solution remains clear and apparently unchanged in spite of the fact that silicic acid is only slightly soluble in water. If the liquid thus obtained is placed in a vessel whose walls are formed of parchment paper or of oladder, and this vessel is placed in pure water, it is possible to wash out all the excess hydrochloric acid and all the sodium in the form of sodium chloride. This is the so-called process of dialysis. The liquid in the dialyzer contains silicic acid.

The silicic acid, however, is not in the form of a true solution. If it is evaporated, an amorphous, gelatinous mass is obtained which is only slightly soluble in water. The boiling and freezing points of the solution do not differ much from those of pure water. The addition of various substances, especially of salts, causes the liquid to solidify as a jelly, especially if it has been concentrated somewhat by evaporation in the cold.

A similar experiment can be performed with arsenious acid and hydrogen sulfide. The aqueous solution of arsenious oxide turns orange yellow when hydrogen sulfide is passed into it and becomes opalescent without forming any precipitate, although arsenious sulfide is only very slightly soluble in water. The liquid will pass unchanged through an ordinary paper filter. If a little hydrochloric acid or some salt solution is added to the yellow opalescent liquid, a heavy precipitate of arsenious sulfide at once forms.

A liquid in which a very insoluble substance appears to be in solution far beyond its usual degree of solubility, and yet does not show at all the behavior of an ordinary supersaturated solution, is said to contain the substance in *colloidal solution*. Such solutions are very commonly formed with difficultly soluble gelatinous substances. It was formerly thought that such solutions represented true solutions of difficultly soluble substances in the form of a soluble colloidal modification, but more recent observations with the ultramicroscope have indicated that colloidal solutions are really suspensions of minute solid particles. The colloidal condition evidently interferes with the precipitation of insoluble substances, and since most of the separations of analytical chemistry depend on the formation of precipitates, analytical chemistry is chiefly concerned with the colloidal condition as one that is to be avoided as much as possible.

The suspended particles of most colloids carry electrical charges; a potential difference exists between the particles and the liquid. Sometimes the charge on the particles is positive, as with the colloidal solu-

tions of ferric hydroxide, aluminum hydroxide, and chromium hydroxide; and sometimes the charge is negative, as with the colloidal solutions of silicic acid, stannic acid, the sulfides of arsenic and cadmium, silver iodide, silver chloride, gold, platinum, and silver. Substances in the colloidal condition which carry an electric charge are precipitated by an electrolyte. Negatively charged colloids are precipitated by the action of positive ions, and, conversely, the positively charged colloids are precipitated by negative ions. The precipitated substance carries with it a little of the precipitating ion in the form of an adsorption compound. The precipitating power of electrolytes increases decidedly with the valence of the precipitating ion.

Some colloids do not carry much of an electric charge, and sometimes the charge is positive in acid and negative in alkaline solutions. Colloids which do not carry much electric charge are not precipitated by dilute solutions of electrolytes. These colloids are coagulated by heat, by any other method of dehydration such as the addition of concentrated salt solutions, or by the addition of another solvent such as alcohol. Colloids which are not sensitive to precipitation by electrolytes often act as protective colloids and hinder the precipitation of other substances. Thus tannic acid, gelatin, and albumin act as such protecting agents, probably by forming protective films.

To prevent the colloidal condition in analytical work it is necessary to take certain precautions. Since electrolytes cause the precipitation of colloids, it may be expected that their absence will tend to aid in the formation of colloidal solutions. Thus in washing a precipitate which is known to have a tendency to pass into colloidal solution, it is best to wash with a solution of some indifferent electrolyte rather than with pure water. Again, if precipitations are attempted in very dilute solutions of such substances as arsenious sulfide, it is best to have an electrolyte in the solution at the start. It is also necessary to remember that the colloids carry down with them the precipitating ion by which they are coagulated. To avoid analytical mistakes caused by such loss of ions, a sufficient concentration of some other ion is usually provided in the form of an acid or an ammonium salt. The washing of the precipitated colloid with ammonium chloride or ammonium nitrate gradually removes these precipitated ions but it is very difficult to avoid all danger of loss from this source.

When protective colloids, especially of the gelatin or albumin type, are present, they may interfere so much with the common precipitation tests that it is necessary to destroy the protective colloid, usually by oxidation, before proceeding with the analysis.

In estimating the dimensions of small particles, such as molecules or ions in solution or colloids in a state of suspension, it is customary to use three units which are much smaller than the millimeter — the *micron*, the *millimicron*, and the *Ångström:*

$$1 \text{ micron} = 1\ \mu = 10^{-3} \text{ mm}$$
$$1 \text{ millimicron} = 1\ \text{m}\mu = 10^{-6} \text{ mm}$$
$$1 \text{ Ångström} = 1\ \text{Å} = 10^{-7} \text{ mm} = 0.1\ \text{m}\mu$$

The Greek letter μ is used, therefore, to represent one-millionth of a meter or one-thousandth of a millimeter. Some writers have used the symbol $\mu\mu$ to mean the millimicron, but this practice has been frowned upon and is more likely to lead to confusion.

For very small weights of material the unit γ (gamma) is often used; it is 0.001 mg.

A very large molecule such as that of starch dissolves in water in particles which may be 5 mμ in diameter, but the solution of starch shows some of the properties of a colloid. In general, we may say that the ions or molecules dissolved by water are rarely larger than 1 mμ in diameter if held in true solution. The ions, although they are hydrated, usually have diameters of a few Ångström units. If an aqueous solution of an electrolyte is illuminated by a powerful beam of light, there is no scattering of the light when the solution is viewed at right angles to the direction of the beam. If particles larger than 10 mμ are suspended in water, such a scattering of the light is observed (Tyndall effect). With the ultramicroscope, therefore, the presence of particles larger than 10 mμ can be detected, but what we really see is not the individual particles but their diffraction images. With an ordinary microscope particles smaller than 0.25 μ cannot be detected.

The colloidal state is characterized by particles whose dimensions vary between 1 mμ and 0.1 μ. If the particles in water are larger than 0.1 μ, it is customary to speak of a *suspension*, but the actual lines between a true solution, a colloidal solution, and a suspension can only be drawn arbitrarily as the state of true solution (molecular dispersion) tends to overlap the state usually recognized as that of a colloid and there is no hard and fast line to draw between a colloidal solution and a mere mechanical suspension.

Arsenic trisulfide is very slightly soluble in water. It has been estimated that only about 0.5 mg will dissolve in 1 l of water. On the other hand, by shaking very finely divided arsenic sulfide with water, or by saturating a solution of arsenious oxide with hydrogen sulfide, it is possible apparently to dissolve as much as 10 g of As_2S_3. The solution will appear clear when viewed in transmitted light but will appear turbid in reflected light; *i.e.*, it looks clear when the test tube is held to the light and one looks through it but appears turbid if one holds the test tube down and views the liquid with the light that is reflected from it.

The physical properties of a true solution (osmotic pressure, lowering of the freezing point, raising of the boiling point, etc.), are determined by the concentration of the solution. A colloidal solution, on the other hand, shows but little depression of the freezing point or rise of the boiling point as compared with the pure solvent.

There are two types of colloids. Some show little, if any, attraction for water. Their solutions are only slightly viscous, and if flocculated by the addition of an electrolyte the particles settle out in a condition easy to filter. Such colloids are called *suspensoids* of *hydrophobic* (lyophobic) colloids. The colloid held in suspension is called a *sol*. When flocculated it is a *gel*. Most of the difficultly soluble inorganic precipitates, such as the metal sulfides, ammonium phosphomolybdate, silver iodide, etc., will yield sols of this type. The second type of colloid has a marked affinity

for water and is called an *emulsoid* or *hydrophylic colloid*. Relatively large quantities of electrolyte are required to cause flocculation; the precipitate adsorbs water strongly, and the colloidal solutions are very viscous. Organic compounds such as the proteins and higher carbohydrates belong to this class, as do silicic acid and aluminum hydroxide. The gels of this type are very hygroscopic, and the last traces of moisture are hard to remove upon ignition; silica and alumina are examples. The ignited residue is also hygroscopic.

Flocculation and Peptization. Colloidal solutions are to be avoided in analytical chemistry because the suspended material cannot be removed by filtration through a paper filter. When flocculated, the particles have a large surface and great adsorptive power. The finely divided particles can be kept in suspension by adsorption of ions, whereby the colloid assumes an electric charge. If a cation is adsorbed the charge is positive, and if an anion is adsorbed the charge is negative. The ions which determine the original charge on the surface of the colloid usually remain during, and sometimes after, the flocculation. The flocculated colloids, however, usually undergo an aging effect which decreases the total surface and the amount of adsorption.

Every precipitate has a tendency to adsorb one of its own ions. Thus the metal sulfides have strong adsorptive powers toward sulfide ions, and silver halides for both silver and halogen ions. Whenever adsorption takes place, there must be adsorption of some other ion to preserve electroneutrality. When a sulfide precipitate adsorbs sulfide ions primarily, it also adsorbs hydrogen ions secondarily. The primary ions adsorbed are held firmly to the surface of the colloid, but the other ions, which may be called *counter ions*, will stay at some distance from the surface although in its vicinity. The electrostatic forces between the negative ions adsorbed on the surface of a sulfide precipitate and the positive hydrogen ions are very large, and an electrical double layer is set up between the particles and the solution. The existence of this double layer is responsible for the stability of the colloid. All the particles of colloid have the same charge and cannot approach closely to one another. If this double layer is destroyed, the particles will come together and form larger particles. The double layer can be destroyed by the addition of a suitable quantity of electrolyte, and flocculation results. The actual quantity of electrolyte required varies. Thus to flocculate arsenic trisulfide sol, 103 equivalents of NaCl, 1.31 equivalents of $CaCl_2$, and only 0.062 equivalent of $AlCl_3$ are required.

In washing a colloidal precipitate with water, some of the adsorbed ions may be removed. Then, if the concentration of this ion in the wash water is below the concentration required to effect flocculation, the particles may go back into the sol condition. This is called *peptization*, and it can be prevented by washing the precipitate with a suitable electrolyte.

Sometimes the adsorption property of a colloid can be used to advantage. Thus hydrous stannic oxide in dilute nitric acid solution will adsorb H_3PO_4 and H_3AsO_4 so strongly that, when sufficient of the colloid is present, all the H_3PO_4 and H_3AsO_4 can be removed from solution.

Precipitates thrown down from very dilute or from very concentrated solutions are in the form of very fine crystals. Thus when barium sulfate is precipitated from solutions which are above 0.75 N in concentration or less than 0.001 N, the precipitate is so finely divided that it has colloidal properties and cannot be removed by ordinary filtration. The precipitates are so fine that they appear to be amorphous.

Aging of Precipitates. Very fine precipitates will often become filterable if allowed to stand for some time in contact with the mother liquor. Keeping the solu-

tion near the boiling point often helps, and the addition of a little filter paper pulp is recommended. When the precipitation takes place from fairly concentrated solutions the crystals form so quickly that they are imperfect. On standing the crystals tend to perfect themselves; particles dissolve from the imperfect places and are deposited elsewhere. Small particles have a slightly greater solubility than larger particles; the small particles dissolve and are deposited upon the larger ones. Sometimes the precipitate that forms first is a metastable modification which, on standing, is changed to a more stable and less soluble state.

Coprecipitation. Precipitates are rarely perfectly pure. They contain mother liquor to some extent and often substances which are normally soluble under the conditions prevailing. Thus when barium sulfate is formed by adding barium chloride to a solution of potassium sulfate, the precipitate contains a little potassium which is very hard to remove by washing, although potassium sulfate is easily dissolved by water. We say that the potassium is coprecipitated with the barium sulfate. Coprecipitation is sometimes due to adsorption on the surface of the precipitate. The adsorption of foreign ions on the surface of a precipitate is sometimes called occlusion to distinguish it from inclusion which results from some of the mother liquor being entrapped by the crystal while it is forming. Sometimes a *solid solution* (also called *mixed crystals*) is formed of two substances which have the same crystalline character. Thus $PbSO_4$ sometimes crystallizes with $BaSO_4$ to form an apparently homogeneous mass or "single phase."

Postprecipitation. Many precipitates are deposited slowly and the solution is in a state of supersaturation for a long time. Thus, when calcium oxalate is precipitated in the presence of considerable magnesium, the precipitate is practically pure at first, but if it is allowed to remain in contact with the solution, magnesium oxalate forms slowly and the presence of the calcium precipitate tends to hasten the formation of the magnesium oxalate. Similarly with the sulfides; some sulfides are precipitated very slowly by hydrogen sulfide, but the presence of some other sulfide often hastens the precipitation. Thus when hydrogen sulfide is passed into a solution of zinc in 0.1*N* hydrochloric acid, no precipitate of zinc sulfide forms until after standing a long time. If, however, mercury or copper ions are present in the solution the precipitate of copper or mercury sulfide which results causes the zinc sulfide to form much more rapidly than it otherwise would. This is probably due to the fact that the sulfides have strong adsorptive powers toward hydrogen sulfide, thus increasing the hydrogen sulfide concentration at the surface of the precipitate.

The Evaporation of Acids

It is often necessary to diminish the acid concentration of a solution. The simplest way to accomplish this is by neutralization, but it is often undesirable to introduce foreign substances into the solution; in such cases the acid is removed by evaporation. To prevent loss by spattering, it is well to evaporate in a porcelain dish on the steam bath; but, to save time, the evaporation may take place over a free flame. In this case the solution should be kept in motion either by stirring or by rotating the contents of the dish and moving it back and forth over the flame. For evaporations over a free flame, an Erlenmeyer flask is often used; the sides of the flask, being cooled by the air, act as a condenser and delay evaporation, but they also serve to

prevent mechanical loss. Spattering is caused by steam being formed too rapidly at the bottom of the dish, by steam being formed beneath a crust which has formed on the surface of the liquid, or by steam being formed from enclosed mother liquid in a solid that has separated. The steam escapes then only after its pressure has become considerable. The breaking of glass dishes when heated over a free flame is due to overheating the glass by contact of the flame with some part that is not being kept relatively cool by contact with liquid. Moving the vessel back and forth over the flame prevents breakage by preventing overheating of the glass; the bottom is kept uniformly wet on the inside even when but little liquid remains.

The behavior of acids upon evaporation is interesting. A solution of hydrochloric acid of specific gravity 1.10 boils at 110° under atmospheric pressure. The solution contains 20.2 per cent of hydrogen chloride, and its concentration is thus a little less than 6 *N*. No other mixture of water and hydrochloric acid boils as high, and consequently in evaporating a solution of hydrochloric acid, although the total quantity of hydrochloric acid constantly diminishes, the concentration of the remaining acid will tend to approach the composition of the constant-boiling mixture. If the acid is more dilute at the start, evaporation will cause the acid that remains to be more concentrated, and if more concentrated at the start, evaporation will cause the remaining acid to be more dilute.

Nitric acid similarly forms a constant-boiling mixture with water. This mixture boils at 120.5° and contains 68 per cent of nitric acid; the acid concentration of the mixture is about 15.5 *N*.

Sulfuric acid forms with water a constant-boiling mixture that contains 98.3 per cent of anhydrous sulfuric acid and boils at 330°. It was once thought that these constant-boiling mixtures of acid and water corresponded to definite hydrates of the acid, but the composition of such a mixture and the boiling point vary with changes in pressure in a way that proves that no definite compound is present.

When it is desired to change a solution of a chloride to one of a nitrate it is very easy to do this by evaporating once or twice with nitric acid. The nitric acid reacts with the hydrochloric acid,

$$6\,HCl + 2\,HNO_3 \rightarrow 4\,H_2O + 2\,NO\uparrow + 3\,Cl_2\uparrow$$

and by adding an excess of the nitric acid all the chloride is decomposed. The most economical way to accomplish the change is to evaporate nearly to dryness and then add a little strong nitric acid, repeating the evaporation and addition of acid until no more red fumes are evolved on adding the acid (NO + air = red NO_2).

Similarly a solution of nitric acid may be changed to one of hydrochloric acid. Aqua regia* is formed, as in the above reaction, and by using an excess of hydrochloric acid all the nitrate is decomposed.

The replacement of nitric acid or of hydrochloric acid by sulfuric acid is based on another principle. This change is accomplished by evaporating till dense fumes of sulfuric acid are evolved. Very little sulfuric acid is lost until all the more volatile acid has evaporated.

Phosphoric acid is still less volatile. By evaporation with phosphoric acid even sulfuric acid can be distilled off without losing an appreciable quantity of phosphoric acid, but the phosphoric acid is changed to pyrophosphoric acid or to metaphosphoric acid.

To change a sulfate or a phosphate solution to a chloride or nitrate presents a more difficult problem than that of simple evaporation. It is customary to remove the phosphate or sulfate ions by precipitation or to precipitate the desired cation as hydroxide or carbonate and to dissolve the precipitate in the desired acid.

Filtration and Washing of Precipitates

When a precipitate is produced in qualitative analysis it is necessary to remove it from the liquid by means of *filtration*. The size of the filter used should be determined by the size of precipitate and not by the volume of liquid. In attempting to detect the presence of traces of a substance it is often necessary to work with large quantities of the original substance, and this involves the use of correspondingly large volumes of liquid. If from such a solution a very little precipitate is formed, it will be practically lost if spread over a large filter, and further work with the precipitate is hampered.

Before such a precipitate is examined it must be completely freed from all traces of the filtrate. This is accomplished by *washing*. Washing must be continued until no test can be obtained with the wash water for a certain substance known to be present in the filtrate. For example, suppose that it is necessary to filter off some suspended barium sulfate from a solution containing sodium sulfate; the precipitate must be continually washed until a sample of the wash water, acidified with hydrochloric acid, no longer gives a precipitate on the addition of barium chloride. As a rule, it is not advisable to run the wash water into the filtrate, because this occasions an unnecessary dilution of the filtrate. The filter must always be smaller than the funnel, and the precipitate should not extend higher than to within 5 mm of the top of the

* Aqua regia is the name given to a mixture of three volumes of concentrated hydrochloric acid and one volume of concentrated nitric acid.

filter. Finally, large precipitates should be avoided as far as possible, for they render exact work more difficult — filtration and washing consuming too much time.

II. Reactions in the Dry Way

These reactions are employed chiefly in the so-called "preliminary examination," in testing the purity of precipitates, and in the examination of minerals. The most important reactions of this nature consist in the testing of a substance with regard to its

1. Fusibility
2. Ability to color the non-luminous Bunsen flame
3. Volatility
4. Behavior toward oxidation and reduction.

In order to carry out these reactions it is customary to use the non-luminous gas flame; and to understand the operations to be described it is necessary for us to know something about the composition of illuminating gas and the nature of the flame.

Illuminating gas, when made by the destructive distillation of coal, contains about 1.6 per cent CO_2, 4.0 per cent C_nH_{2n} compounds (illuminants), 0.4 per cent O_2, 8.5 per cent CO, 49.8 per cent H_2, 29.5 per cent CH_4, 3.2 per cent C_2H_6, and 3.2 per cent N_2.

All these components, except CO_2, O_2, and N_2 (which are present only in small amounts), are combustible; they are reducing substances. Illuminating gas ordinarily burns with a luminous flame, and the luminosity is due to the presence of unsaturated hydrocarbons (C_nH_{2n}), principally ethylene, propylene, acetylene, etc. If ethylene is heated to a certain temperature, it is decomposed into methane and carbon:

$$C_2H_4 \rightarrow CH_4 + C$$

and it is glowing carbon which causes the luminosity of the flame.

The other unsaturated hydrocarbons behave like ethylene. The remaining combustible constituents of illuminating gas burn with a non-luminous flame. If we bring air into the gas, the flame becomes non-luminous. With the Bunsen burner air is introduced by opening the holes at the base of the burner. In such a gas flame there are, according to Bunsen, the following parts (Fig. 1*):

I. *The inner cone* of the flame, *aab*, in which no combustion takes place, because the temperature here is too low. This part of the flame contains unburned gas mixed with about 62 per cent of air.

* In the drawing, the lines *d* represent a metallic chimney, or *flame protector*, which rests upon the support *ee*. It is advisable to furnish each burner with such a flame protector.

II. *The flame mantle,* indicated by *acaba,* which is composed of burning gas and air.

III. *The luminous tip,* at *b,* which does not appear unless the air-holes are partly closed.

In these three principal parts of the flame Bunsen distinguished six reaction zones:

1. *The base of the flame at* α'. The temperature here is relatively low, because the burning gas is cooled by the constant current of fresh air, and also because the burner itself conducts away considerable heat. This part of the flame serves to test volatile substances to see whether they impart color to the flame. If several substances are present which color the flame, it is often possible to observe the colors one after the other, in that the most volatile substance colors the flame first, and later the colors caused by the less volatile ones are seen. This would not be possible at a hotter part of the flame, as all the substances would then be immediately volatilized, producing a mixture of colors.

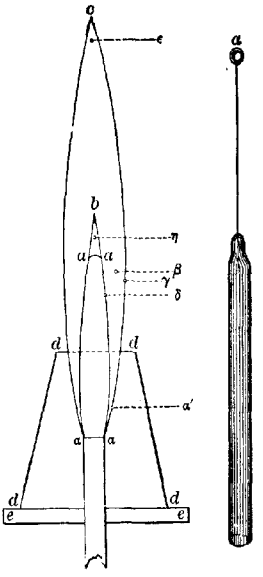


FIG. 1

2. *The fusing zone at* β. This lies at a distance of somewhat more than one-third of the height of the flame, and equidistant from the outside and the inside of the mantle, which is broadest at this part. Since this is the hottest part of the flame, it serves for testing substances as to their fusibility and volatility.

3. *The lower oxidizing flame* lies in the outer border of the fusing zone at γ, and is especially suited for the oxidation of substances dissolved in vitreous fluxes.

4. *The upper oxidizing zone,* at ϵ, consists of the non-luminous tip of the flame, and acts most effectively when the air-holes of the lamp are fully open. It is used for various oxidizing tests, the roasting away of volatile products of oxidation, and generally for all processes of oxidation where the very highest temperature is not required.

5. *The lower reducing zone* lies at δ, in the inner border of the fusing zone next to the dark cone. Since the reducing gases are mixed here with oxygen from the air, many substances which are reduced by the upper

reducing flame are unaffected in this zone. This part of the flame is consequently very well adapted for a test which cannot be made with the blowpipe, namely, reduction on the charcoal stick, and in vitreous fluxes.

6. *The upper reducing flame* is at η, in the luminous tip of the dark inner cone which may he produced by gradually diminishing the supply of air. If the luminous tip has been made too large, a test tube or porcelain dish filled with water and placed over it will be blackened, which should never be the case. This luminous tip contains no free oxygen, is rich in separated incandescent carbon, and has, therefore, a much stronger reducing action than the lower reducing zone. It is used more particularly for the reduction of oxides collected in the form of incrustations.

Methods for the Examination of a Substance in the Dry Way

1. Test of the Fusibility

This test is principally made in the examination of minerals, which are introduced into the flame in the loop of a platinum wire (about as thick as a horschair). The sample is examined, after heating, by means of a magnifying glass to see whether the corners are rounded, as the result of melting. The potentially hottest temperature of the fusing zone amounts to about 2300° C.* It will never be possible to reach this temperature with the test, because the substance itself loses heat by radiation. Since the amount of heat lost by radiation is proportional to the surface exposed, it is evident that we will obtain the maximum heat by using a very small sample and holder. For this reason a coarse wire should not be used for this test.

We distinguish the following degrees of heat:

1. Faint red glow	525° C	Melting point of magnesium.	651°
2. Dark red glow	700°	aluminum..	658.7°†
3. Bright red glow	950°	silver	960.5°
4. Yellow glow	1100°	gold	1063°
		copper	1083°
5. Faint white glow	1300°	nickel	1452°
6. Full white glow	1500°	platinum	1773°

Below 525° C the following substances melt: tin at 232°, bismuth at 271°, lead at 327°, zinc at 420°.

---

* This temperature will be considerably lower with too large a supply of air. According to Naumann, the temperature of illuminating gas with 1½ times its volume of air reaches about 1818° C, but the temperature obtained is usually much lower owing to loss by radiation. The finest platinum wire can be melted by means of the flame, but not when it is as thick as a horsehair.

† Circular 35 of the Bureau of Standards, Washington, D. C. Cf. Burgess-Le Chatelier: "High-Temperature Measurements."

2. Color Imparted to the Flame

The substance (best in the form of the chloride) is placed in the loop of a fine platinum wire, moistened with hydrochloric acid, introduced into the base of the flame, and then finally brought into the fusing zone.

3. Test of the Volatility

A little of the substance is heated in a small test tube or in a piece of glass tubing sealed at one end. Volatile substances are transformed into vapor, often without melting, and the vapors condense on the cooler walls of the tube.

4. Oxidation and Reduction

(a) *In Vitreous Fluxes or Beads*

To make a bead, borax ($Na_2B_4O_7 \cdot 10\,H_2O$) or salt of phosphorus ($NaNH_4HPO_4 \cdot 4\,H_2O$) is used. A piece of very fine platinum wire, about 3 cm long, is sealed into the end of a glass tube. The wire is heated to redness, and then quickly dipped into the borax or salt of phosphorus, held near the flame, whereby a small amount of the salt is fused to the end of the wire. By repeated heating and dipping into the salt a bead of sufficient size is obtained. This should be about 1.5 mm in diameter at the most. It is not advisable to make a loop

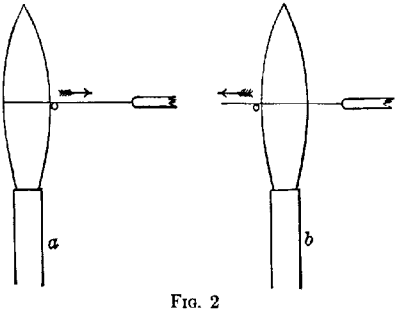


Fig. 2

at the end of the wire, because in this way the exposed surface is unnecessarily increased. There is no danger of the bead falling off, provided the wire is held horizontally in the flame and the bead is not too large. In order to bring the substance in question into the bead, it is only necessary to moisten the bead with the tongue, and then dip it into the finely powdered substance, which will cause a small amount to adhere to the bead. It is preferable to introduce too little substance

into the bead rather than too much, because, in the latter case, the bead will become dark and opaque. The oxidation of the substance in the bead is brought about by heating it in the lower oxidizing flame; reduction is usually effected by heating in the lower reducing zone, and cooling in the dark inner cone, in order to prevent oxidation, which might take place if the substance were cooled in the air.

In order to clean the wire, a borax bead is produced on the wire, which is then heated, as shown in Fig. 2, *a*, on one side of the bead only, so that the latter runs along the wire in the opposite direction, dissolving off all impurities. By heating the bead from the other side, Fig. 2, *b*, it is driven toward the end of the wire, from which it can be shaken off by a quick jerk. By repeating this process three times the wire is cleaned with the exception of a small amount of adhering borax-glass, which can be removed by heating the wire in the fusing zone until the sodium flame entirely disappears.

(*b*) *Reduction on the Charcoal Stick*

These exceedingly beautiful reactions are among the most sensitive of those used in analytical chemistry and should be faithfully practiced by every beginner. The cause of their sensitiveness is due to their taking place on the extreme end of a tiny piece of charcoal, that is at a *point*, so that the sample has no opportunity to spread itself over a large surface, which is the case with the ordinary reactions on charcoal before the blowpipe.

To carry out these reactions, we use an ordinary splinter consisting of good, straight fibers, such as used in an old-fashioned brimstone match (not a safety match, which has already been subject to chemical treatment). It is impregnated with sodium carbonate (soda) in the following manner: A crystal of sodium carbonate ($Na_2CO_3 \cdot 10\,H_2O$) is warmed in the flame, whereby it melts in a part of its water of crystallization. Three-fourths of the length of the match is now smeared with this liquid soda, and the match is then slowly rotated on its axis in the flame, until the soda melts and penetrates the charcoal. On withdrawal from the flame there should be no place which continues to glow; if there is such a place, the stick should be quickly immersed in the soda again. In this way one obtains a little solid piece of charcoal, which can be heated for a long time without burning through.

In order to carry out a reduction, a small amount of the substance to be examined is mixed on the palm of the hand with an equal amount of anhydrous sodium carbonate, a small drop of melted sodium carbonate crystal is added, and the mixture is made into a paste by means of the blade of a penknife. The heated piece of charcoal is then rubbed

into the mixture, which adheres to it. The sample is first heated in the lower oxidizing flame until it has melted, and then moved into the lower reducing flame. The reduction will be made evident by a violent swelling up of the melt, caused by the evolution of carbon dioxide. As soon as the mass melts quietly the reduction is complete. The substance is allowed to cool in the dark cone, after which it is removed from the flame. The metal is now found on the extreme end of the carbonized match, concentrated in a point. This point is broken off and triturated with a small amount of water in an agate mortar. The excess of sodium carbonate goes into solution, part of the charcoal floats on the surface of the water, while the heavier metal sinks to the bottom. If the reduced metal is iron, nickel, or cobalt, it will not be noticeable to the eye, but it may be taken up with a magnetized knife-blade, to which it will adhere, usually mixed with charcoal. This should be dried by cautious warming, the tuft of metal taken off, rubbed between the thumb and forefinger, and then brought into contact with the knife again, to which only the metal will now adhere. The metal is then transferred to a piece of ashless filter paper about 3–4 mm wide and 50 mm long, so that it comes as near as possible to the end of the strip. By means of a capillary tube, a drop of hydrochloric acid and one of nitric acid are added, and the paper is warmed over the flame until the black speck (the metal) has disappeared, when the final test can be made.

In order to test for iron, a drop of potassium ferrocyanide is added, whereby the presence of iron is shown by the appearance of a distinct formation of Prussian blue. To test for nickel and cobalt, the metal is dissolved in nitric acid, the excess of acid is evaporated off, and a drop of concentrated hydrochloric acid added, whereby the paper is colored blue if cobalt is present; the nickel shows at the most only a very weak greenish color — usually, however, no color. A little caustic soda solution is now added, and the paper held in the vapors of bromine; if either nickel or cobalt is present a brownish black spot appears, due to the formation of either $Ni(OH)_3$ or $Co(OH)_3$.

If, however, the metal reduced was malleable, it is usually obtained in the form of a metallic globule on the end of the stick, where it can be examined with the aid of a lens. Copper is not always obtained as a globule, but usually as a reddish sintered mass. By pressing down on a malleable metal in the agate mortar it is obtained as a glistening fragment, which can be readily separated from the specifically lighter charcoal by washing. To accomplish this the agate mortar is inclined and a stream of water is directed sidewise upon the mass, whereby the charcoal is washed out with the water, and the metal is left clean. It is transferred to a watch glass and tested as follows:

1. *The Metal is White* (Pb, Sn, Ag, Pt). The metal is treated with a few drops of nitric acid and carefully warmed. Lead and silver dissolve readily, particularly upon addition of a little water. Silver will be detected by the addition of a drop of hydrochloric acid, whereby white silver chloride, soluble in ammonia, is precipitated. The test for lead is dilute sulfuric acid, which precipitates white lead sulfate.

If the metal, on treatment with nitric acid, remains unchanged, it is probably platinum. It should be dissolved in aqua regia, evaporated to dryness, dissolved in a little water, and potassium chloride solution added. A yellow, crystalline precipitate confirms the presence of platinum. If the metal, when treated with nitric acid, becomes changed into a white, insoluble oxide, it is tin. In this case, another fragment of metal is dissolved in concentrated hydrochloric acid and tested for tin by means of mercuric chloride solution, or by adding sodium hydroxide and a very little bismuth nitrate solution (p. 169, §6).

2. *The Metal is Yellow to Red* (Cu, Au). Copper is readily dissolved in nitric acid, and the solution gives with potassium ferrocyanide a reddish brown precipitate. Gold is insoluble in nitric acid, but soluble in aqua regia. The evaporated solution gives a violet-brown color with stannous chloride, due to finely divided gold.

(*c*) *Reduction in a Glass Tube*

Besides the borax bead and the charcoal stick, reduction is often effected by means of metallic sodium, potassium, or magnesium.

Thus small amounts of phosphorus in anhydrous salts may be detected in the following manner: The substance to be tested is placed in a glass tube, 3 mm wide and 50 mm long, which is closed at one end. A small cylinder of potassium or sodium (freed from petroleum by rubbing between filter paper), or even a piece of magnesium wire, is added to the tube, and the contents then heated until the glass itself begins to soften. The reaction is so violent that the substance seems to take fire. After cooling, the tube is broken in a porcelain mortar, when by breathing over the mass, the smell of phosphoretted hydrogen may be detected.

The halogens, sulfur, and nitrogen are tested for in a similar way, as will be shown later.

(*d*) *Reduction in the Upper Reducing Flame for the Purpose of Forming Metallic and Oxide Incrustations*

The volatile elements which are reducible by means of hydrogen or charcoal may be detected in this part of the flame with the greatest ease, as, for example, arsenic, antimony, cadmium, bismuth, selenium, and

tellurium. The metallic incrustations are obtained by holding in one hand a small portion of the substance on a thin asbestos thread (platinum will be attacked) in the upper reducing zone of a small gas flame, where the oxide is reduced to volatile metal, and burned in the upper oxidizing flame to oxide. In the other hand, closely over the substance to be tested, is held a glazed porcelain evaporating dish, filled with water, as is indicated in Fig. 3 at *B*. The metallic vapors are condensed by the cold dish, and deposited on it in the form of a metallic mirror or film. If, however, the dish is held above the upper oxidizing flame (at *A*), there is formed a thin, often invisible, oxide incrustation on the bottom.

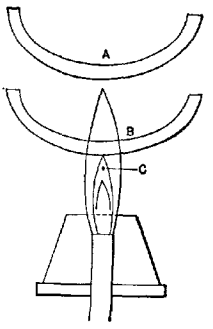


FIG. 3

Should it be necessary to treat the metallic incrustation with a large amount of solvent (as is necessary in the detection of selenium and tellurium), the porcelain dish is replaced by a test tube half filled with cold water. A somewhat larger test tube is used to hold the solvent, and the smaller test tube, on which the incrustation was deposited, is placed within the larger tube and the liquid warmed if necessary.

(*e*) *Blowpipe Reduction on Charcoal*

These tests are made in the so-called "preliminary examination." For this purpose a small cavity is made with a penknife in a piece of good charcoal (preferably of linden wood), in which a knife-bladeful of the substance to be tested is placed, previously mixed with twice as much anhydrous sodium carbonate. Since charcoal is a porous substance, it will readily absorb melted substances, such as a salt of the alkalies. Other substances are changed, by means of the sodium carbonate used, into carbonates, which are, for the most part, decomposed, on heating, into oxides and carbon dioxide. The oxides of the noble metals are decomposed, without the aid of the charcoal, into oxygen and metal; those of the remaining metals are either reduced to metal or remain unchanged. Thus CuO, PbO, Bi_2O_3, Sb_2O_3, SnO_2, Fe_2O_3, NiO, and CoO are reduced either to a fused metallic globule (Pb, Bi, Sb, Sn, Ag, and Au), or to a sintered mass of metal (Cu), or to a glistening metallic fragment (Fe, Ni, Co, Pt). The oxides of zinc, cadmium, and arsenic do not give metallic globules, but are, however, easily reduced to metal. These metals are so volatile that they are changed into vapors, and are carried from the reducing zone of the flame into the oxidizing zone,

where they are changed into difficultly volatile oxides. These oxides, which have characteristic colors, are then deposited on the charcoal outside the cavity.

Zinc gives an incrustation which is yellow while hot and white when cold; that of cadmium is brown; the oxide of arsenic gives a white and readily volatile incrustation. Furthermore, the volatilization of arsenic gives rise to a characteristic garlic-like odor. The metals lead, bismuth, and tin give, besides the metallic globule, an oxide incrustation which is typical.

At the same time, nitrates, nitrites, chlorates, etc., may be recognized by the fact that they cause a very rapid combustion of the glowing charcoal (deflagration). This deflagration is not to be confused with a decrepitation which takes place on heating substances containing enclosed moisture or gases, such as rock salt, fluorspar, etc. Crystals of such substances are burst by the quick expansion of the enclosed liquid, and scattered about.

Many difficultly fusible substances do not melt into the charcoal. Thus many silicates form a bead with the soda, which only after *continuous* heating will give up the alkali and allow it to be absorbed by the charcoal, leaving behind the white infusible silica. Phosphates and borates act similarly, only these do not leave behind an oxide, but a fused glass. Infusible white oxides, as those of calcium, strontium, magnesium, aluminum, and many of the rare earths (Welsbach mantle, for example), glow very brightly, and in fact more brightly as they are more strongly heated.

Spectrum Analysis

If a ray of white light is passed through a glass prism, not only is the direction of the ray changed, but the white light is decomposed into colors; it suffers dispersion. It will be found that the red rays are deflected least and the violet rays most. The picture obtained — the spectrum — if projected on a screen (Fig. 4), does not show the colors sharply separated, but merging into one another. Such a spectrum is called a continuous, or uninterrupted, spectrum. *Every glowing solid or liquid body emits white light; the spectra obtained in all such cases will be continuous ones.* Glowing vapors and gases behave quite differently. They do not emit white

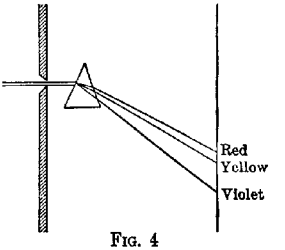


FIG. 4

light, but light composed of rays of definite wave lengths, which are characteristic for each gas and for each vapor. The light emitted from glowing vapors or gases, when decomposed by the prism, yields on the screen a *discontinuous* or *interrupted spectrum*. If the light is passed through a fine slit before reaching the prism, the spectrum will be found to consist of a greater or less number of colored lines which always ap-

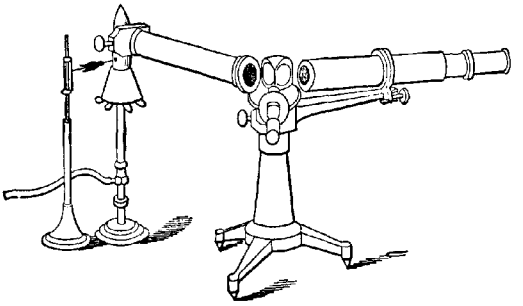


FIG. 5

pear in the same place with any given substance, provided the prism or its position is not changed. To determine the exact position of these lines, Bunsen and Kirchhoff made use of a spectroscope similar to that shown in Fig. 5. A cross section of the apparatus is shown in Fig. 6.

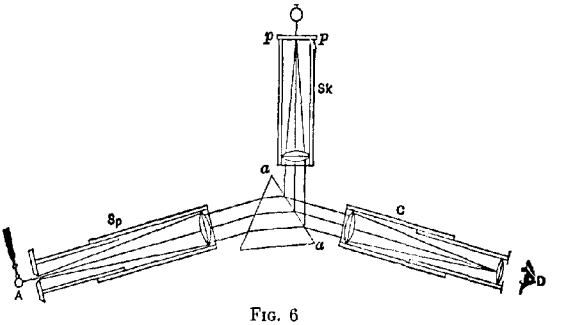


FIG. 6

The substance to be examined is placed in the loop of a platinum wire and introduced at *A* into the non-luminous gas flame, by means of which it is volatilized. The rays of light pass through the slit into the

collimator tube *Sp*, reach the prism, by which the rays are refracted into the telescope *C*, and are observed at *D*. Upon a glass plate at the end of the tube *Sk* is a transparent scale, which is illuminated by a small flame at *B*. This tube is so inclined toward the face *aa* of the prism that the rays of light from this tube are totally reflected into the tube *C*, and reach the eye of the observer; thus the rays from the substance appear at a certain position on the scale. However, as the position of the lines depends upon the dispersive power of the prism and upon its angle of refraction, it is clear that the position of the lines may be somewhat different in different spectroscopes. As every ray has a definite wave length, it is better to give the wave lengths of the rays which appear, rather than their position on the scale.

Wave lengths are expressed in millionths of a millimeter called millimicrons and designated as $m\mu$, or in Ångström units, abbreviated Å, $1\ \mu = 0.001$ mm, $1\ m\mu = 0.001\ \mu$, 1 Å $= 0.1\ m\mu$.

The following values give the wave lengths of various lines in the spectrum:

Red rubidium line	Rb_δ	$= 795.0\ m\mu$
rubidium line	Rb_γ	$= 781.1\ m\mu$
potassium double line	K_α	$= 766.9\ m\mu$ $= 766.5\ m\mu$
lithium line	Li_α	$= 670.8\ m\mu$
cadmium line*	Cd_γ	$= 643.9\ m\mu$
Orange-yellow lithium line	Li_β	$= 610.8\ m\mu$
Yellow sodium (middle of the double line)	Na	$= 589.3\ m\mu$
Green calcium line	Ca_β	$= 554.4\ m\mu$
thallium line	Tl	$= 535.0\ m\mu$
cadmium line*	Cd_α	$= 508.6\ m\mu$
Blue cadmium line*	Cd_β	$= 480.0\ m\mu$
cadmium line*	Cd_γ	$= 467.8\ m\mu$
strontium line	Sr_δ	$= 460.7\ m\mu$
cesium line	Cs_β	$= 459.3\ m\mu$
cesium line	Cs_α	$= 455.5\ m\mu$
Blue-violet indium line	In_α	$= 451.1\ m\mu$
Violet rubidium line	Rb_β	$= 421.5\ m\mu$
rubidium line	Rb_α	$= 420.2\ m\mu$
indium line	In_β	$= 410.1\ m\mu$
potassium line	K_β	$= 404.4\ m\mu$
H (Fraunhofer C line)		$= 396.8\ m\mu$

* The cadmium lines can be seen distinctly only in spark spectra.

In the earlier models, the spectroscope did not have a scale graduated in terms of wave lengths. Thus the sodium line appeared at division 50 instead of at a graduation marked 589.3. If, however, the wave lengths are plotted as ordinates and the corresponding scale divisions as abscissas, a plot can be obtained from the readings for the characteristic lines of say K_α, K_β, Li_α, Na, Tl, Sr_δ, In_α and In_β and their known wave which will show the wave length corresponding to any position on the scale. The modern instruments, however, give the wave length of any line to within 0.2 mμ.

To obtain a sharply defined spectrum, the instrument must be adjusted so that the rays enter the telescope when it is adjusted for parallel rays, as can be accomplished by focussing it upon some distant object. The collimator tube must be lengthened or shortened until the picture of the slit is sharply defined and the scale tube adjusted until the scale is clearly defined. The direct vision pocket spectroscope, with an arrangement of prisms as shown in Fig. 7, is useful in the laboratory when it is desired to make a quick test for alkali or alkaline earth cation.

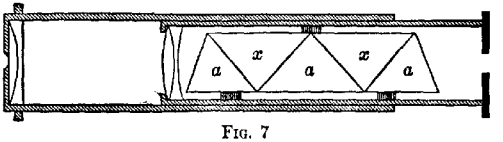


FIG. 7

It is not possible to volatilize all substances in the gas flame but by means of an electric spark most substances can be volatilized sufficiently to give spark spectra. To accomplish this Bunsen attached platinum wires to conical pieces of charcoal which were soaked with the solution to be tested. Then by passing an electric spark through the two carbon points, enough of the salt was volatilized to give a spark spectrum which could be viewed in the spectroscope. Some of the lines, however, are then caused by the carbon electrodes and some by the air. To avoid this a solution of the salt can be used as anode and an iridium wire as cathode, nearly touching the surface of the liquid in a so-called *fulgurator*. As little as 0.002 mg of calcium can be detected in 1 ml of solution in this way. In the case of metals, sometimes it is made one of the electrodes in an electric arc or a little powdered sample is placed in a cavity of the lower electrode of an arc.

To examine gas spectra, small Geissler tubes are used which contain the gas to be detected.

Besides flame spectra and spark spectra, *absorption spectra* are sometimes useful. If white light is passed through a colored solution or a

gas, certain rays are absorbed and if the light is then viewed through a spectroscope, these rays will be missing. A bright light will be seen broken by black bands which are characteristic of different substances. Thus solutions of permanganate, neodymium, praseodymium, erbium and many other substances give characteristic absorption spectra and the dark Frauenhofer lines in the spectrum of the sun tell us what elements are present in the atmosphere of the sun. The absorption spectrum of the blood of a mouse which has died from carbon monoxide poisoning is characteristic and in this way the presence of carbon monoxide has often been detected.

A spectroscope capable of use for spectrum analysis was first made available by Kirchhoff and Bunsen at about 1860. The discovery, with its aid, of cesium (1860), rubidium (1861), thallium (1861), and indium (1863) promptly showed what a potent instrument it was for research.

In many problems, time may be saved and error avoided by the use of spectroscopy to supplement the ordinary methods of chemical analysis, for example: 1. Rapid qualitative analyses for all the metallic constituents of a substance as a basis for planning the chemical analysis. 2. Approximate analyses by examination with a visual instrument. 3. Examination of precipitates for freedom from constituents which should have been separated. 4. Testing the purity of analytical reagents. 5. Detection of rare, unexpected, or trace metals in minerals. 6. Analyses of substances of which only very small quantities are available. 7. Check control of metallurgical factory output.

For visual use, one of the "Wave-length" forms is desirable. Various sizes are made; the one usually selected is shown in Fig. 8, but to deal adequately with substances which contain considerable quantities of Fe, Mn, Ni, Pt, Ti, and other metals having complex spectra a larger instrument is needed.*

Although the wave-length spectrometer is a very useful instrument for such problems as are mentioned above, most of the work in an industrial laboratory calls for a quartz spectrograph (*viz.*, an apparatus for photographing the spectrum). It is true that the chemist can often,

* Of textbooks written by practical spectroscopists the following deserve special mention:

Spectroscopy in Science and Industry, S. Judd Lewis, Blackie & Sons, Ltd., London and Glasgow.

The Practice of Spectrum Analysis, F. Twyman, F.R.S., and a number of collaborators.

Wavelength Tables for Spectrum Analysis, F. Twyman, F.R.S., and D. M. Smith, A.R.C.S., B.Sc., Adam Hilger, Ltd., London.

Bibliography of Literature on Spectrum Analysis, D. M. Smith, British Non-Ferrous Metals Research Association, London, 1935.

by merely looking through a spectroscope, assure himself of the presence or absence of a particular metal, but the spectrograph is generally more useful — first because most of the distinctive and sensitive spectral lines lie in the ultra-violet part of the spectrum, which is invisible to the eye; secondly, because a permanent record is obtained; and thirdly, because

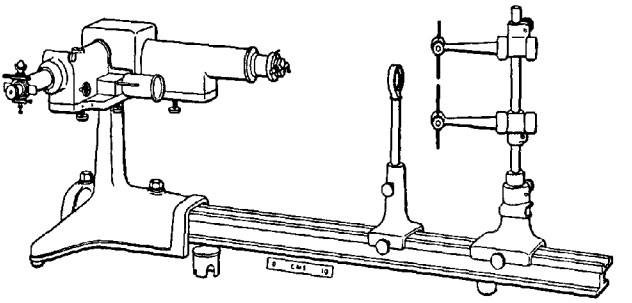


FIG. 8

a spectrogram of a sample can be quickly taken by any intelligent laboratory assistant and the chemist can then carry out the examination of the photograph at his leisure.

A modern quartz spectrograph is shown in Fig. 9, and Fig. 10 shows a typical analysis made with its aid.

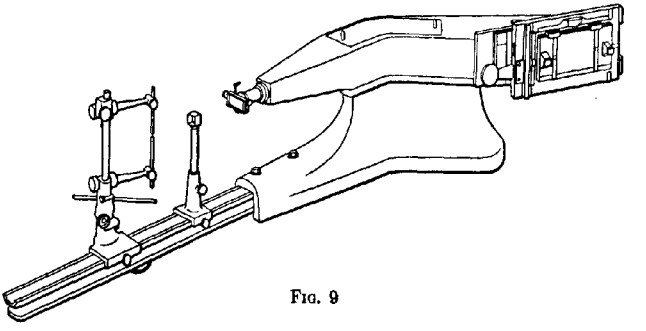


FIG. 9

In Fig. 10, the bottom spectrum is of zinc supposed to be pure, the middle is a of sample of zinc spelter under examination, and the top is of cadmium, the metal whose presence or absence is to be determined. By seeking in the middle spectrum lines which are absent from the bottom,

but strongly present in the top, one finds by the presence of the sensitive cadmium lines 3261·1, 3406·6, 3466·2, and 3610·5 that the spelter contains some cadmium. The two lines 3247·5 and 3274·0 which appear in all three spectra are the *raies ultimes* of copper, showing that

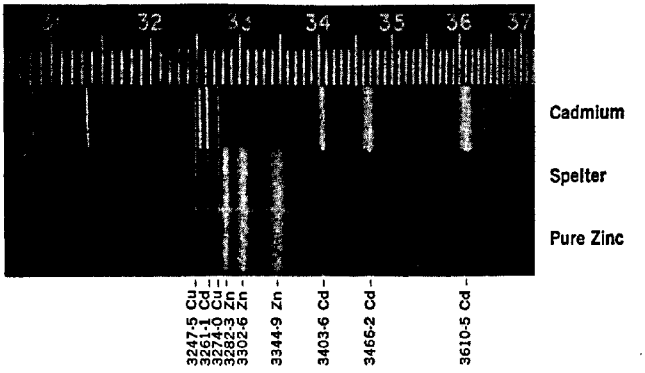


FIG. 10

even the supposedly pure zinc is not free from a small quantity of this impurity. Lead is present in both the cadmium and spelter, but not in the pure zinc, as shown by the lines 3683·5 and 3639·6. A small quantity of silver is present in all three samples. The silver line 3382·9 appears faintly in the three spectra, but the line 3280·7, which is present in the spectrum of the cadmium, is masked by the strong zinc line 3282·3 in the two zinc spectra.

Division of the Metals into Groups

The metals, for purposes of analytical chemistry, are usually divided into five groups:

The *First Group* contains those metals whose *chlorides are insoluble*, or difficultly soluble, and whose sulfides are insoluble, in dilute acids. They may, therefore, be precipitated from their solutions by means of either hydrochloric acid or hydrogen sulfide.

The *Second Group* contains those metals whose chlorides are soluble, but whose *sulfides are insoluble*, in dilute acids. They may be precipitated from their solutions by means of hydrogen sulfide, but not by hydrochloric acid.

The *Third Group* contains those metals whose *sulfides are soluble in*

dilute acids, but are insoluble in water and alkalies; and also those metals whose sulfides are hydrolytically decomposed into hydrogen sulfide and insoluble hydroxide. The members of this group are precipitated completely by *hydrogen sulfide only from alkaline solutions.*

The *Fourth Group* contains those metals whose sulfides are soluble in water, but whose *carbonates are insoluble in the presence of ammonium chloride.* They are precipitated by *ammonium carbonate* in the presence of ammonium chloride, but not by any of the above reagents.

The *Fifth Group* contains magnesium and the alkalies; they are not precipitated by any of the above reagents. If the ammonium carbonate precipitation is carried out in a concentrated solution containing alcohol, magnesium will be precipitated in the fourth group. This procedure is in some respects advantageous.

This purely arbitrary grouping is based upon certain specific solubilities and does not classify the general chemical behavior of the elements as the periodic system of grouping does. In some cases the members of the analytical group all belong to the same group in the periodic system but this is not usually true. The table on page 87 shows how the elements are grouped in the periodic system. The Roman numerals across the top of the table show the number usually assigned to the group or family. The next horizontal column shows the lowest valence of the family as represented by a typical hydride. Below this is shown the highest valence of the family as represented by a typical oxide. Note that there are eight units difference between the lowest negative valence and the highest positive valence of the element in a given family. The heavy number in front of the symbol of the element is the so-called *atomic number*. It represents the number of excess positive charges on the nucleus of the atom and is the same as the number of electrons rotating about the nucleus of the free atom. The chemical properties of the elements are due, it is believed, to the number of these electrons and the way they are arranged about the nucleus.

In order to carry out an analysis with certainty it is necessary to understand not only the reactions of the different elements, but also the *sensitiveness* of each reaction. The analyst should be able to draw a conclusion by the size of the precipitate formed as to the approximate amount which is present in the original substance. This, however, is possible only when the experiments are made with known amounts. *Consequently reagents of a known strength are used and allowed to act on known amounts of the different substances.* According to the suggestion of R. Blochmann* it is well to make the solutions of the different reagents either double-normal, normal, half-normal, or tenth-normal. For many years the author has used in his laboratory solutions of reagents and salts according to this principle, and has found that the beginner in this way gets a far better understanding of the stoichiometrical relations than when solutions of almost any concentration are used, as was formerly the custom.

By a *normal* solution is understood one which contains in a liter one gram equivalent of the substance in question, referred to a gram atom of hydrogen as a unit. A tenth-normal solution will contain one-tenth of a gram equivalent in a liter, etc.

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* *Berichte*, 1890, 31.

PERIODIC TABLE OF THE ELEMENTS

Groups		0	I	II	III	IV	V	VI	VII	VIII
Hydrides			RH	RH_2	RH_3	RH_4	RH_5	RH_6	RH	
Oxides			R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	
Period	Series		1 H 1.008							
I	1	2 He 4.00	3 Li 6.94	4 Be 9.02	5 B 10.82	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	
II	2	10 Ne 20.18	11 Na 23.00	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 31.02	16 S 32.06	17 Cl 35.46	
III	3	18 A 39.94	19 K 39.10	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.84 · 27 Co 58.94 · 28 Ni 58.69
	4		29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.92	
IV	5	36 Kr 83.7	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 96.0	43 Ma?	44 Ru 101.7 · 45 Rh 102.9 · 46 Pd 106.7
	6		47 Ag 107.88	48 Cd 112.41	49 In 114.8	50 Sn 118.7	51 Sb 121.76	52 Te 127.6	53 I 126.92	
V	7	54 Xe 131.3	55 Cs 132.91	56 Ba 137.36	57 La 138.92	58 Ce 140.13 · 59 Pr 140.9 · 60 Nd 144.27 · 61 Il · 62 Sm 150.4 · 63 Eu 152.0 · 64 Gd 156.9 · 65 Tb 159.2 · 66 Dy 162.5				
	8		67 Ho 163.5	68 Er 167.6 · 69 Tm 169.4	70 Yb 173.0 · 71 Lu 175.0	72 Hf 178.61	73 Ta 180.88	74 W 184.0	75 Re 186.3	76 Os 191.5 · 77 Ir 193.1 · 78 Pt 195.2
VI	9		79 Au 197.2	80 Hg 200.61	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210.0)	85 Alabamine 221.0	
	10	86 Rn 222	87 Vi	88 Ra 226.0	89 Ac (226)	90 Th 232.1	91 Pa (231)	92 U 238.07		

Thus one liter of a normal solution will contain

$$\left.\begin{aligned} HCl &= 36.47\ g \\ \frac{H_2SO_4}{2} &= \frac{98.08}{2} = 49.04\ g \\ \frac{H_3PO_4}{3} &= \frac{98.05}{3} = 32.68\ g\ * \\ NaOH &= 40.01\ g \\ \frac{KMnO_4}{5} &= \frac{158.03}{5} = 31.61\ g\ \dagger \\ \frac{K_2Cr_2O_7}{6} &= \frac{294.2}{6} = 49.02\ g\ \ddagger \end{aligned}\right\} \text{equivalent to one gram atom of hydrogen}$$

The great advantage of this system is that one always knows how much of one solution should be used in order to react with another quantitatively. Thus 1 ml of a normal caustic soda solution will neutralize 1 ml of any normal acid, or 2 ml of any half-normal acid. In the same way 1 ml of a normal solution of sulfuric acid, or of any sulfate, will precipitate quantitatively the barium from 1 ml of a normal barium chloride solution.

The Laboratory Reagents

I. Concentrated Acids

	Sp. gr.	Per cent by Wt.	Approx. Conc.
Acetic acid, glacial	.....	99.5	17 *N*
Formic acid	.....	27	6 *N*
Hydrobromic acid	1.49	48	9 *N*
Hydrochloric acid	1.19	37.9	12 *N*
Hydrofluoric acid	1.14	48	27 *N*
Nitric acid	1.42	69.8	16 *N*
Perchloric acid	.....	60	9 *N*
Phosphoric acid	1.7	85.0	15 *N*
Sulfuric acid	1.84	96.0	36 *N*

* Assuming that the three hydrogen atoms are replaceable (cf. p. 11).

† This is considering the solution as an oxidizing agent. As a precipitant, the normal solution of $KMnO_4$ would contain one mole per liter. The reagent is almost invariably used an an oxidizing agent and not as a precipitant.

‡ Also considered as an oxidizing agent. As a precipitant, the normal solution of $K_2Cr_2O_7$ used to form $PbCrO_4$ or $BaCrO_4$ would contain one-fourth mole per liter.

II. Diluted Acids

	Sp. gr.	Per cent by Wt.	Approx. Conc.
Acetic acid	1.047	35.0	6 *N*
Hydrochloric acid	1.10	20.0	6 *N*
Nitric acid	1.20	32.3	6 *N*
Perchloric acid	.....	.....	6 *N*
Silicotungstic acid $H_8SiO_6 \cdot 12\ WO_3 \cdot 22\ H_2O$	.....	42	*N*
Sulfuric acid	1.18	24.8	6 *N*
Sulfurous acid	(satd. soln. of SO_2)		0.33 *N*
Tartaric acid	(150 g per liter)		2 *N*

III. Bases

	Sp. gr.	Per cent by Wt.	Approx. Conc.
Ammonium hydroxide	0.90	28% NH_3	15 *N*
Ammonium hydroxide	0.96	9.9% NH_3	6 *N*
Barium hydroxide	(satd. soln. $Ba(OH)_2 \cdot 8\ H_2O$)		0.4 *N*
Potassium hydroxide	1.37	36.9	9 *N*
Sodium hydroxide	1.22	19.7	6 *N*

IV. Salts

(*a*) *Ammonium Salts*

Name of Salt	Directions for Making Reagent	Conc.
Ammonium acetate $NH_4C_2H_3O_2$ or NH_4Ac	Mix equal volumes of 6-normal acetic acid and 6-normal ammonia.	3 *N*
Ammonium carbonate $(NH_4)_2CO_3$	Dissolve 250 g freshly powdered ammonium carbonate in 1 l 6-normal NH_4OH. The commercial salt is $NH_4HCO_3 \cdot NH_4CO_2NH_2$.	6 *N*
Ammonium chloride NH_4Cl	Dissolve 54 g in 1 l of water.	*N*
Ammonium chloride	290 g per liter.	Satd.
Ammonium molybdate $(NH_4)_2MoO_4$	Dissolve 90 g of pure ammonium molybdate in 100 ml of 6-normal NH_4OH, add 240 g of NH_4NO_3, and dilute to 1 l. The formula of the commercial salt is $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$.	*N* (3 *N* in NH_4NO_3)
Ammonium oxalate $(NH_4)_2C_2O_4$	Dissolve 35 g $(NH_4)_2C_2O_4 \cdot H_2O$ in 1000 ml water.	0.5 *N*
Ammonium polysulfide $(NH_4)_2S_x$	Digest 1 l 6-normal ammonium monosulfide with 25 g flowers of sulfur for some hours and filter.	6 *N*
Ammonium sulfide $(NH_4)_2S$	Pass H_2S into 200 ml 15-normal NH_4OH in a bottle immersed in running water or in ice water until no more gas is absorbed; then add 200 ml 15-normal NH_4OH and dilute to 1 l.	6 *N*

(*b*) *Other Salts*

Name of Salt	Formula	Formula Weight	Grams per Liter	Conc.
Barium chloride	$BaCl_2 \cdot 2\,H_2O$	244	122	*N*
Cadmium nitrate	$Cd(NO_3)_2 \cdot 4\,H_2O$	308	154	*N*§
Calcium chloride	$CaCl_2 \cdot 6\,H_2O$	219	110	*N*
Calcium sulfate	$CaSO_4 \cdot 2\,H_2O$	172	2.6	Satd.
Cobalt nitrate	$Co(NO_3)_2 \cdot 6\,H_2O$	291	437	3 *N*
Cobalt nitrate	$Co(NO_3)_2 \cdot 6\,H_2O$	291	44	0.3 *N*
Ferric chloride	$FeCl_3 \cdot 6\,H_2O$	270	90	*N**
Ferric nitrate	$Fe(NO_3)_3 \cdot 9\,H_2O$	404	135	*N*
Lead acetate	$Pb(C_2H_3O_2)_2 \cdot 3\,H_2O$	379	190	*N*
Lead nitrate	$Pb(NO_3)_2$	331	165	*N*
Mercuric chloride	$HgCl_2$	272	27	0.2 *N*
Mercurous nitrate	$Hg_2(NO_3)_2 \cdot 2\,H_2O$	561	280	*N*
Potassium bichromate	$K_2Cr_2O_7$	294	49	*N*†
Potassium chromate	K_2CrO_4	194	291	3 *N**
Potassium cyanide	KCN	65	65	*N*
Potassium ferricyanide	$K_3[Fe(CN)_6]$	329	110	*N**
Potassium ferrocyanide	$K_4[Fe(CN)_6] \cdot 3\,H_2O$	422	105	*N**
Potassium iodate	KIO_3	214	75	0.35 *N* as salt
Potassium iodide	KI	166	166	*N*
Potassium nitrite	KNO_2	85	510	6 *N*
Potassium oxalate	$K_2C_2O_4 \cdot H_2O$	184	276	3 *N*
Potassium permanganate	$KMnO_4$	158	10	0.3 *N*†
Potassium thiocyanate	KCNS	97	97	*N*
Silver nitrate	$AgNO_3$	170	17	0.1 *N*
Sodium acetate	$NaC_2H_3O_2 \cdot 3\,H_2O$	136	136	*N*
Sodium arsenite	$NaAsO_2$	130	130	*N*
Sodium bicarbonate	$NaHCO_3$	84	84	*N*
Sodium bisulfite	$Na_2S_2O_5$	190	190	4 *N*
Sodium bromide	$NaBr \cdot 2\,H_2O$ or NaBr	139 or 103	69 or 51	0.5 *N*
Sodium carbonate	Na_2CO_3	106	159	3 *N*
Sodium nitrite	$NaNO_2$	69	210	3 *N*‖
Sodium phosphate	$Na_2HPO_4 \cdot 12\,H_2O$	358	119	*N*
Sodium sulfate	$Na_2SO_4 \cdot 10\,H_2O$	322	160	*N*
Sodium thiosulfate	$Na_2S_2O_3 \cdot 5\,H_2O$	248	124	0.5 *N*‡
Uranyl acetate	$UO_2(C_2H_3O_2)_2 \cdot 2\,H_2O$	424	21	0.1 *N*

* As precipitant. † As oxidizing agent. ‡ As reducing agent.

§ This reagent must be free from sulfate.

‖ If the salt contains chloride mix with 1 per cent of its volume of silver nitrate and filter after shaking. Note on the label that the reagent contains $AgNO_3$.

V. Special Reagents

Antimony trichloride, 6-molar: Dissolve 137 g of $SbCl_3$ in enough 6 *N* HCl to make 100 ml.

Bismuth nitrate, approx. 4 *N*: Completely saturate 6 *N* acetic acid with $Bi(NO_3)_3 \cdot 5H_2O$.

Bromine, liquid: Use the c.p. product.

Chloroplatinic acid: Dissolve 26.5 g $H_2[PtCl_6] \cdot 6\,H_2O$ (corresponding to 10 g Pt) in enough water to make 100 ml of solution.

Dimethylglyoxime: Dissolve 12 g of the solid in 1 l of 95 per cent ethyl alcohol.

Ether saturated with HCl: Saturate anhydrous ether at 0° with dry HCl gas.

Ferrous sulfate, 2 *N*: Dissolve 280 g $FeSO_4 \cdot 7H_2O$ in 500 ml of 6 *N* sulfuric acid and keep in contact with iron nails.

Hydrogen peroxide, 1-molal: Use the c.p. 3 per cent solution.

Hydroxylamine hydrochloride: 3-molal: Dissolve 21 g of $NH_2OH \cdot HCl$ in enough water to make 100 ml.

Magnesium ammonium chloride, *N* in $MgCl_2$: Dissolve 100 g $MgCl_2 \cdot 6H_2O$ and 100 g NH_4Cl in water, add 50 ml 15-normal NH_4OH, and dilute to 1 l.

Magnesium ammonium nitrate, 1-normal in $Mg(NO_3)_2$, 3-normal in ammonium nitrate: Dissolve 130 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 240 g NH_4NO_3 in water, add 35 ml of 6-normal NH_4NO_3, and dilute to 1 l.

Magnesium uranyl acetate: Treat separately 8.5 g of uranyl acetate and 50 g of magnesium acetate, each with 6 ml of glacial acetic acid and 95 ml of water, heating at 70° until clear solutions are obtained. Mix at this temperature, allow to cool, and filter after standing two hours at 20°.

Mercury, liquid.

Methyl violet: Dissolve 1 mg of indicator in 25 ml of 95 per cent alcohol and 75 ml of water.

Potassium antimonate: Add 22 g of the best commercial salt to 1 l of boiling water, boil until nearly all the salt has dissolved, cool quickly, add 35 ml of 10 per cent KOH solution, and filter after standing over night.

Potassium carbonate, 50 per cent: Dissolve 100 g of K_2CO_3 in 100 ml of water.

Potassium mercuric iodide, 0.5-normal in K_2HgI_4: Dissolve 115 g HgI_2 and 80 g KI in enough water to make the volume 500 ml; add 500 ml 6-normal NaOH and decant the solution from any precipitate that may form on standing. The stock solution should be kept in the dark. For sensitive work the water used, as well as the solids, must be absolutely free from ammonia.

Sodium acid tartrate: Use a saturated solution of the c.p. salt.

Sodium cobaltinitrite, 1-molar in $Na_3Co(NO_2)_6$: Dissolve 207 g of c.p. $NaNO_2$ and 291 g of $Co(NO_3)_2 \cdot 6H_2O$ in 500 ml of water, add 10 ml of 6 *N* acetic acid, and let the mixture stand at least 24 hours. Filter and dilute to 1 l. Prepare not more than a few weeks before it is to be used.

Sodium 6-chloro-5-nitrotoluenemetasulfonate, saturated: Saturate 100 ml of water with salt prepared as described by Schultz and Lucas, *J. Am. Chem. Soc.*, **49**, 298 (1927).

Sodium hypobromite, NaBrO: Prepare as needed by taking 2 ml of Br_2-water and adding 6 *N* NaOH until the solution is yellow and then as much more NaOH.

Sodium sulfide, 3-normal in Na_2S, 1-normal in Na_2S_2, and 1-normal in NaOH. Dissolve 480 g of $Na_2S \cdot 9H_2O$ and 40 g of NaOH in water, add 16 g of sulfur, shake until all the S is dissolved, and dilute to 1 l.

Stannous chloride, 1-normal: Dissolve 115 g of $SnCl_2 \cdot 2H_2O$ in 170 ml 12-normal HCl, dilute to 1 l, and keep in bottles containing a strip of pure tin.

Starch and potassium iodide: Rub 20 g soluble starch to a thin paste with a little water in a mortar and pour the paste into 1 l of boiling water. Boil five minutes and filter through a loose plug of cotton wool. Add 10 g KI and 5 ml chloroform to the filtrate.

Thiourea: Dissolve 100 g of the solid in 1 l of water.

Turmeric: Shake turmeric powder with 95 per cent alcohol and filter.

Urea: Dissolve 200 g urea in 1 l 6-normal HCl.

VI. Saturated Solutions

	1000 ml water dissolves
Barium hydroxide	68 g $Ba(OH)_2$ at 20°
Bromine water	32.68 g Br_2
Calcium sulfate	2.6 g $CaSO_4 \cdot 2\ H_2O$
Chlorine water	6.5 g Cl_2
Hydrogen sulfide	4.2 g H_2S
Lime water	1.3 g CaO
Sulfurous acid	106 g SO_2

VII. Special Solvents

Amyl alcohol
Carbon disulfide
Carbon tetrachloride
Chloroform
Ethyl acetate
Ethyl alcohol (99 per cent)
Ethyl ether
Methyl alcohol (free from acetone)

Gases

Chlorine: Prepare by dropping 12 *N* HCl on $KMnO_4$ crystals.

Hydrogen chloride: Prepare by dropping concentrated sulfuric acid, 5–10 ml at a time, through a thistle tube upon 100 g of sodium chloride until 100 ml of acid have been added. Thereafter, warm the mixture but do not heat above 80°. Use a small-bore delivery tube for the escape of the gas and have the thistle tube just dip into a short test tube filled with sulfuric acid which rests in the evolution flask.

Sulfur dioxide: Prepare by dropping 18 *N* sulfuric acid on $Na_2S_2O_5$.

Hydrogen sulfide: Prepare from ferrous sulfide, FeS, and 6 *N* H_2SO_4 or 6 *N* HCl.

VIII. Solid Reagents

Absorbent cotton
Aluminum turnings
Ammonium chloride, NH_4Cl
Ammonium nitrate, NH_4NO_3
Antimony, powder
Asbestos fiber, for filters
Barium carbonate, $BaCO_3$
Bismuth dioxide, may be used in place of sodium bismuthate
Borax, $Na_2B_4O_7 \cdot 10\ H_2O$
Boric acid, H_3BO_3
Calcium chloride (anhydrous)
Calcium oxide, CaO
Calcium phosphate, $Ca_3(PO_4)_2$
Chloride of lime, $CaOCl_2$
Copper wire or turnings
Ferrous sulfate, $FeSO_4 \cdot 7\ H_2O$
Ferrous sulfide, FeS
Glass wool
Iron nails, Fe
Iron powder
Lead (finely granulated), Pb
Lead dioxide (free from Mn), PbO_2
Litmus paper, blue
Litmus paper, red
Paraffin
Potassium acid sulfate (fused), $KHSO_4$
Potassium carbonate, K_2CO_3
Potassium chlorate, $KClO_3$
Potassium dichromate, $K_2Cr_2O_7$
Potassium ferricyanide, $K_3Fe(CN)_6$
Potassium iodide, KI
Potassium nitrate, KNO_3
Quartz powder
Salicylic acid
Silica (precipitated), SiO_2
Silver carbonate, Ag_2CO_3
Silver sulfate, Ag_2SO_4
Sodium acetate, $NaC_2H_3O_2$
Sodium ammonium phosphate (microcosmic salt), $NaNH_4HPO_4 \cdot 4\ H_2O$
Sodium bicarbonate, $NaHCO_3$
Sodium bismuthate, $NaBiO_3$
Sodium bitartrate, powdered
Sodium carbonate, Na_2CO_3
Sodium nitrate, $NaNO_3$
Sodium nitrite, highest purity
Sodium peroxide, Na_2O_2
Sodium nitroprussiate, $Na_4[Fe(CN)_5NO] \cdot 2\ H_2O$

Sodium sulfide, $Na_2S \cdot 9\ H_2O$
Sodium tetraborate (see Borax)
Sulfur, flowers
Starch $(C_6H_{10}O_5)x$
Tartaric acid, $H_2C_4H_4O_6$
Tin (pure foil)
Zinc (finely granulated) 20 mesh

Reactions of the Elements

This valuable tabulated summary of the characteristic reactions of the elements is taken, for the most part, from the excellent work of Noyes and Bray, *Qualitative Analysis for the Rare Elements*.

It shows the behavior of the characteristic cations, arranged according to the Periodic Classification (see p. 87), toward dilute hydrochloric acid, dilute sodium hydroxide in excess, and the more important oxidizing agents and reducing agents. The table also shows the forms in which the elements are obtained in the final identification tests.

A formula in heavy type indicates that a solid is formed, but if the solid is fairly soluble in water the formula is printed both in heavy type and in plain type. Heavy type is not used, however, in the formulas for the precipitates obtained in the final tests. Colors are given if the solids or solutions are not white or colorless.

Under the reactions with HCl, the formation of a complex acid is shown only when the element probably is obtained chiefly in this form. When two symbols of complexes are given, the form obtained with dilute acid is given first, then that obtained with stronger acid.

Under the reactions with NaOH, the formulas of precipitates are not given if they dissolve in excess alkali hydroxide.

As regards the behavior with reducing agents and oxidizing agents, it is assumed that the solution is normal in HCl, unless otherwise stated, and the agent added is present at a low concentration. The reducers chosen are Zn, $SnCl_2$, H_2S, SO_2, dilute HI, $FeCl_2$, hot 7–9 *N* HBr and hot 6–12 *N* HCl.

The reducing action of these agents generally decreases in the order named, and metallic Sn reacts like Zn unless otherwise stated. When the lowest valence state is not reduced by Zn, dashes are inserted. It may be assumed, unless otherwise stated, that, when a low valence state is reduced by a given agent, a higher state will also be reduced. As oxidizers, Cl_2, Br_2, I_2, air, and hot 2–3 *N* HNO_3 (with no chloride present) are considered. Dashes are inserted when chlorine causes no oxidation.

In stating the sensitiveness of some of the tests described, the Greek letter γ *will be used to represent a micromilligram* (0.001 *mg*).

To save space and to accustom the student to reading them, the following abbreviations adopted by the editors of *Chemical Abstracts* are often used in the text:

AcO^-	acetate ion	contg.	containing	pptn.	precipitation
addn.	addition	decompn.	decomposition	qual.	qualitative
alc.	alcohol	dil.	dilute	sat.	saturate
alk.	alkaline	examn.	examination	satd.	saturated
anal.	analysis	expt.	experiment	sepn.	separation
aq.	aqua	g	gram or grams	sol.	soluble
at. wt.	atomic weight	insol.	insoluble	soln.	solution
calc.	calculate	l	liter	soly.	solubility
compd.	compound	mixt.	mixture	*Sp*	soly. product
conc.	concentration	ml	milliliter(s)	temp.	temperature
concd.	concentrated	*N*	normal	vol.	volume
const.	constant	ppt.	precipitate	wt.	weight

REACTIONS OF THE ELEMENTS IN THEIR VARIOUS VALENCE STATES

Group	Element	Valence State	Compounds Formed with 0.1–1.0 *N* HCl	Compounds Formed with 0.1–1.0 *N* NaOH	Reduced in Acid Solution by	Oxidized in Acid Solution by	Precipitated as
I	Li	1	LiCl	LiOH	.....	.....	Li_3PO_4
	Na	1	NaCl	NaOH	.....	.....	NaCl; NaH_2SbO_4; $NaMg(UO_2)_3(AcO)_9$
I_a	K	1	KCl	KOH	.....	.....	$KClO_4$; $K_2NaCo(NO_2)_6$, yellow
	Rb	1	RbCl	RbOH	.....	.....	$RbClO_4$; $RbHC_4H_4O_6$; $Rb_2NaBi(NO_2)_6$, yellow
	Cs	1	CsCl	CsOH	.....	.....	$CsClO_4$ $CsSb_2Cl_7$ $Cs_8SiW_{12}O_{42}$
I_b	Cu	1	**CuCl**, $HCuCl_2$	{Cold, **CuOH**, yellow Hot, Cu_2O	Zn	{Cl_2, Br_2, Air, HNO_2, H_2O_2	Cu, red
		2	$CuCl_2$, light blue	{Cold, **Cu(OH)**$_2$, blue Hot, **CuO**, black	Cu, Sn^{++}, SO_2, HI	.....	$Cu_2Fe(CN)_6$, red
	Ag	1	**AgCl**	Ag_2O, brown-black	Zn, Sn^{++}, $HCHO_2$ slowly	.....	Ag black; AgBr light yellow; AgCl
	Au	3	$AuCl_3$, yellow	$NaAuO_2$, yellow	Zn, Cu, Sn^{++}, Fe^{++}, SO_2, $HCHO_2$, $H_2C_2O_4$	.....	Au, purple or black
II	Be	2	$BeCl_2$	$NaHBeO_2$	.....	.....	$Be(OH)_2$; $BeCO_3 xBe(OH)_2$
	Mg	2	$MgCl_2$	**Mg(OH)**$_2$	.....	.....	$MgNH_4PO_4$
II_a	Ca	2	$CaCl_2$	**Ca(OH)**$_2$, Ca(OH)$_2$	.....	.....	CaC_2O_4; $CaSO_4$
	Sr	2	$SrCl_2$	Sr(OH)$_2$, Sr(OH)$_2$	.....	.....	$SrCrO_4$, yellow; $SrSO_4$
	Ba	2	$BaCl_2$	Ba(OH)$_2$	.....	.....	$BaCrO_4$, yellow; $BaSO_4$

II_b	Zn	2	$ZnCl_2$	$NaHZnO_2$	.....	.....	ZnS
	Cd	2	$CdCl_2$	$Cd(OH)_2$	.....	.....	CdS, yellow
	Hg	1	Hg_2Cl_2	Hg_2O, black	Zn, Cu, Sn^{++}, $HCHO_2$	Cl_2, Br_2, I_2	Hg, gray; Hg_2Cl_2
		2	$HgCl_2$; H_2HgCl_4	HgO, red	Sn^{++}	.....	$HgINH_2HgO$, orange
III	Al	3	$AlCl_3$	$NaAlO_2$	.....	.....	$Al(OH)_3$; $AlCl_3 \cdot 6H_2O$
III_a	Sc	3	$ScCl_3$	$Sc(OH)_3$	.....	.....	ScF_3; $Sc(OH)_3$
	Y	3	YCl_3	$Y(OH)_3$	.....	.....	$Y(OH)_3$; YF_3
	Ce	3	$CeCl_3$	$Ce(OH)_3$	.....	$HClO_3$ in concd. HNO_3, $NaBiO_3$	$Ce(OH)_3$; CeF_3
		4	$CeOCl_2$, yellow $CeCl_4$, dark red	$Ce(OH)_4$, yellow	Boiling	.....	$Ce(IO_3)_4$, yellow; CeO_2, H_2O_2, orange
	RE (Rare Earths)	3	$RECl_3$, colored or white	RE$(OH)_3$, colored or white	.....	.....	RE$(OH)_3$, REF$_3$, colored or white
III_b	Ga	3	$GaCl_3$	$NaGaO_2$	.....	.....	$Ga(OH)_3$; $Ga_4[Fe(CN)_6]_3$
	In	3	$InCl_3$	$NaInO_2$	Zn, not Sn	.....	In_2S_3, yellow
	Tl	1	TlCl, TlCl	TlOH	Zn, not Sn	Cl_2, Br_2	TlI, light yellow
		3	$TlCl_3$	$Tl(OH)_3$, dark orange	Sn^{++}, Fe^{++}, SO_2, H_2S, HI, HBr, $HCHO_2$	.....	$Tl(OH)_3$, dark orange
IV_a	Ti	3	$TiCl_3$, dark violet	$Ti(OH)_3$, blue-black	.....	Cl_2 Br_2, I_2, Air, HNO_3, H_2O_2	.....
		4	$Ti(OH)_4$, $TiOCl_2$	$Ti(OH)_4$	Zn	.....	TiO_2; $Ti(HPO_4)_2 \cdot H_2O$
	Zr	4	$ZrOCl_2$	$Zr(OH)_4$	.....	.....	$Zr(HPO_4)_2 \cdot H_2O$
	Th	4	$ThOCl_2$	$Th(OH)_4$	.....	.....	ThF_4; $Th(IO_3)_4$
IV_b	Ge	2	$GeCl_2$	$NaHGeO_2$	Zn	Cl_2, Br_2, I_2, Air, HNO_3	.....
		4	GeO_2, $GeCl_4$	$NaHGeO_3$	.....	.....	GeS_2; K_2GeF_6
	Sn	2	$SnCl_2$, $HSnCl_3$	$NaHSnO_2$	Zn, not Sn	Cl_2, Br_2, I_2, Air, HNO_3, H_2O_2	Sn, gray; SnS, brown-black
		4	H_2SnCl_6	$Na_2SnO_3 \cdot 3\,H_2O$	Sn, Sb	.....	SnO_2; SnS_2, yellow
	Pb	2	$PbCl_2$, $PbCl_2$	$NaHPbO_2$	Zn, Sn partially	Cl_2, not Br_2	$PbSO_4$; $PbCrO_4$, yellow
			H_2PbCl_6, yellow	PbO_2, brown	Boiling	.....	.....

REACTIONS OF THE ELEMENTS IN THEIR VARIOUS VALENCE STATES — *Continued*

Group	Element	Valence State	Compounds Formed with 0.1–1.0 *N* HCl	Compounds Formed with 0.1–1.0 *N* NaOH	Reduced in Acid Solution by	Oxidized in Acid Solution by	Precipitated as
V_a	V	2	VCl_2, violet	$V(OH)_2$, violet-gray	.....	Hot water	.....
		3	VCl_3, green	$V(OH)_3$, green	Zn, Sn partially	I_2, Air, HNO_3	.....
		4	$VOCl_2$, blue	$VO(OH)_2$, gray	HI (concd.)	Cl_2, Br_2, H_2O_2	V_2S_4, brown
				$Na_2V_4O_9$, dark yellow			
		5	V_2O_5, dark red	$NaVO_3$	Cu, Sn++, Fe++, H_2S,	.....	NH_4VO_3
			$H_4V_6O_{17}$, yellow	$Na_8HV_6O_{17}$, yellow	SO_2, HI, HBr, HCl, $HCHO_2$		
	Cb	3	$CbCl_3$, violet	?			
		5	$HCbO_3$	$HCbO_3$, $Na_8Cb_6O_{19}$	Zn	.....	$HCbO_3$
	Ta	5	$HTaO_3$	$HTaO_3$, $Na_8Ta_6O_{19}$	.....	.....	$HTaO_3$; $2\,K_2TaF_7 \cdot Ta_2O_5$
V_b	As	3	As_2O_3, $AsCl_3$	$NaAsO_2$	Zn (to AsH_3)	Cl_2, Br_2	As_2S_3, yellow
		5	H_3AsO_4	Na_3AsO_4	Sn++, SO_2, HI, HBr	.....	As_2S_5, yellow; $MgNH_4AsO_4$
	Sb	3	$SbOCl$, H_3SbCl_6	$NaSbO_2$	Zn (to Sb and SbH_3)	Cl_2, Br_2	Sb, black; Sb_2S_3, orange
		5	$HSbO_3$, $HSbCl_6$	$NaSbO_3$	SO_2, HI, HBr	.....	Sb_2O_5
	Bi	3	$BiOCl$, $HBiCl_4$	$BiO(OH)$	Zn	.....	Bi, black; $Bi(OH)_3$ $BiOCl$
VI_a	Cr	2	$CrCl_2$, blue	$Cr(OH)_2$, dark yellow	.....	Hot water, Cl_2, Br_2	.....
		3	$CrCl_3$, dark green	$Cr(OH)_3$, gray-green	Zn	I_2, Air, HNO_3	
				$NaCrO_2$		$HClO_3$ in concd. HNO_3	$Cr(OH)_3$, gray-green
		6	$H_2Cr_2O_7$, orange	Na_2CrO_4, yellow	Sn++, H_2S, SO_2 Fe++, HI, HBr, HCl, $HCHO_2$	.....	$PbCrO_4$, yellow

VI$_a$ (*Con.*)	Mo	3	$MoCl_3$, red	**$Mo(OH)_3$**, black	.....	I_2, Air, HNO_3, Fe^{+++} (partly)	.....
		5	$MoOCl_3$, green	**$Mo(OH)_5$**, brown	Zn	.....	.....
		5–6	$Mo_2O_5 \cdot xMoO_3$, blue	**$Mo(OH)_5$**+Na_2MoO_4	Sn^{++}, HI	Cl_2, Br_2	.....
		6	**MoO_3**, $MoO_3 \cdot HCl$	Na_2MoO_4	H_2S, SO_2Fe^{++} (partly)	.....	MoS_3, black
	W	3, 4	WCl_3, WCl_4, colored	?	.....	.....	WS_2, black
		5	$WOCl_3$, green	**$W(OH)_5$**, brown	Zn	.....	.....
		5–6	**$W_2O_5 \cdot xWO_3$**, blue	**$W(OH)_5$**+Na_2WO_4	.....	Cl_2, Br_2, I_2, Air, HNO_3	$W_2O_5 \cdot xWO_3$, blue
		6	**H_2WO_4**, yellow	Na_2WO_4	Sn^{++}	.....	H_2WO_4, yellow
	U	3	UCl_3, purple	?	.....	H_2O	.....
		4	UCl_4, green	**$U(OH)_4$**, green	Zn	Cl_2, Br_2, I_2, Air, HNO_3	.....
		6	UO_2Cl_2, yellow	**$Na_2U_2O_7$**, yellow	Cu, Sn^{++}, H_2S, SO_2	.....	$UO_2NH_4PO_4$, yellow; $K_2UO_2[Fe(CN)_6]$, dark red
VI$_b$	Se	4	H_2SeO_3	Na_2SeO_3	Zn, Sn^{++}, H_2S, SO_2 Fe^{++}, HI	Cl_2, Cr^{VI}, Mn^{VII}	Cold, Se, red Hot, Se, black
		6	H_2SeO_4	Na_2SeO_4	HBr, HCl (not H_2S, SO_2, Fe^{++})	.....	.....
	Te	4	H_2TeO_3, $TeCl_4$	Na_2TeO_3	Zn, Sn^{++}, SO_2	Cr^{VI}, Mn^{VII}	Te, black
		6	H_6TeO_6	$Na_2H_4TeO_6$	HI, HBr, HCl (not Sn^{++}, SO_2)	.....	.....
VII$_a$	Mn	2	$MnCl_2$	**$Mn(OH)_2$**	.....	.....	.....
		3	H_2MnCl_5, brown	**$Mn(OH)_3$**, brown	Boiling water	Cl_2, $HClO_3$ in concd. HNO_3	.....
		4	**$MnO(OH)_2$**, brown H_2MnCl_6, brown	**$MnO(OH)_2$**, brown	Boiling water	PbO_2, BiO_2 or $NaBiO_3$	MnO_2, black
		6	**$MnO(OH)_2$**, brown $HMnO_4$, purple	Na_2MnO_4, green	Boiling water	.....	.....
		7	$HMnO_4$, purple	$NaMnO_4$, purple	Zn, Sn^{++}, H_2S, SO_2 Fe^{++}, HI, HBr, HCl	.....	.....
VIII$_a$	Fe	2	$FeCl_2$, light green	**$Fe(OH)_2$**, white	.....	Cl_2, Br_2, Air, HNO_3, H_2O_2	.....
		2–3	$FeCl_2$+$FeCl_3$	$Fe(OH)_{2.67}$, green to black	.....	.....	.....
		3	$FeCl_3$, yellow	$Fe(OH)_3$, reddish brown	Zn, Sn^{++}, H_2S, SO_2 HI, $HCHO_2$, slowly	.....	$Fe_4[Fe(CN)_6]_3$, blue; $Fe(OH)_3$, reddish brown

REACTIONS OF THE ELEMENTS IN THEIR VARIOUS VALENCE STATES — *Concluded*

Group	Element	Valence State	Compounds Formed with 0.1–1.0 *N* HCl	Compounds Formed with 0.1–1.0 *N* NaOH	Reduced in Acid Solution by	Oxidized in Acid Solution by	Precipitated as
VIII$_a$ (*Con.*)	Ru	2	$RuCl_2$, dark blue	$Ru(OH)_2$, (color?)	Zn	I_2, HNO_3	Ru, black
		3	H_2RuCl_5, orange-black (?)	$Ru(OH)_3$, black	Sn, H_2S, SO_2	Cl_2, Br_2	Ru_2O_{3-4}, black
		4	H_2RuCl_6, orange-black	Na_2RuO_3, yellow	HI, Fe^{++}, HBr, slowly	$HClO_4$ (fuming) to RuO_4	.....
		6	$H_2RuCl_6+Cl_2$	Na_2RuO_4, orange-red	Does not exist	Does not exist	.....
		7	$H_2RuCl_5+Cl_2$	$NaRuO_4$, dark green	Does not exist	Does not exist	.....
		8	RuO_4, yellow; or $Ru^{IV}+Cl_2$	$Na_2RuO_5 \cdot H_2O$ orange to red	HBr, HCl	.....	.....
	Os	3	H_3OsCl_6, red	$Os(OH)_3$, dark orange	Zn	.....	Os_2S_3, black
		4	H_2OsCl_6, yellow	$Os(OH)_4$, black	Sn^{++}	Cl_2, Br_2, HNO_3	.....
		6	$H_2OsCl_6+OsO_4$	Na_2OsO_4, orange	Does not exist	Does not exist	.....
		8	OsO_4	$Na_2OsO_5 \cdot H_2O$, yellow to orange	HI, HBr, SO_2, Fe^{++}, C_2H_5OH	.....	.....
VIII$_b$	Co	2	$CoCl_2$, pink	Cold, $Co(OH)Cl$, blue Hot, $Co(OH)_2$, pink	.....	KNO_2	CoS, black
		3	$CoCl_3+Cl_2$	$Co(OH)_3$, black	Boiling water	.....	$K_3Co(NO_2)_6$, yellow;
	Rh	3	H_2RhCl_5, H_3RhCl_6 both orange-red	Cold, $NaRhO_2$, yellow Hot, $Rh(OH)_3$, black	Zn	.....	$Co(OH)_3$, black $Rh(OH)_4$, green Rh, black; $RhCl(NH_3)_5Cl_2$, yellow (for Rh 3 valence)
		4	H_2RhCl_6, blue	$Rh(OH)_4$, green	Boiling water	.....	.....
	Ir	3	H_3IrCl_6, olive-green	$NaIrO_2$	Zn	Cl_2	Ir, black
		4	H_2IrCl_6, black	$Ir(OH)_4$, dark blue	Sn^{++}, Fe^{++}, H_2S, SO_2, $HCHO_2$	.....	$Ir(OH)_4$, dark blue; $(NH_4)_2IrCl_6$, red-bl'k
VIII$_c$	Ni	2	$NiCl_2$, green	$Ni(OH)_2$, pale green	.....	.....	Ni salt of dimethyl glyoxime
		3	$NiCl_3+Cl_2$	$Ni(OH)_3$, black	Does not exist	Does not exist	$Ni(OH)_3$, black
	Pd	2	$PdCl_2$, H_2PdCl_4, dark orange	$NaHPdO_2$, light orange	Zn, Fe^{++}, SO_2, $HCHO_2$	Cl_2	Pd, black
		4	H_2PdCl_6, deep red	$Pd(OH)_4$, dark brown	Boiling water	.....	$(NH_4)_2PdCl_6$, orange-red
	Pt	2	H_2PtCl_4, red-black	$Pt(OH)_2$, dark brown	Zn, $HCHO_2$	Cl_2, Br_2	Pt, black
		4	H_2PtCl_6, yellow	$Na_2Pt(OH)_6$	Sn^{++}, HI	.....	$(NH_4)_2PtCl_6$, yellow

PART II. REACTIONS OF THE CATIONS

The separation of the metals into groups (cf. p. 85) is usually based on the varying solubilities of the chlorides, sulfides, hydroxides, and carbonates.

GROUP I. HYDROCHLORIC ACID GROUP:

SILVER, MERCURY, LEAD

Silver, lead, and mercury are the important members of this group. Lead is never found entirely in this group, and mercury is precipitated as chloride only from mercurous salts. Thallous chloride, TlCl, is also precipitated with this group, but this element will be discussed with the rare elements in Part V. The basic chlorides of bismuth and antimony, BiOCl and SbOCl, sometimes precipitate with this group, but these precipitates dissolve easily in an excess of HCl and thus cause little trouble. Under some circumstances tungsten is precipitated from an alkaline solution as hydrated WO_3 upon adding HCl; this will be discussed in Part V.

SILVER, Ag. At. Wt. 107.88, At. No. 47

Density 10.49. M. P. 960.5°. B. P. about 1944°

Occurrence. — Silver occurs both native and combined (chiefly with sulfur, arsenic, and antimony).

Of the silver-bearing minerals the following may be mentioned: horn silver, AgCl; argentite, Ag_2S; pyrargyrite, Ag_3SbS_3; and proustite, Ag_3AsS_3. Silver is also found with tetrahedrite and with galena.

Properties. — Silver owes its name to the Anglo-Saxon word *seolfor* and its symbol to the Latin word *argentum*. It is a white metal, harder than gold and softer than copper. Its vapor, or a very thin layer of the metal, shows a violet tint. At the melting point it absorbs more than 20 times its own volume of oxygen, and on cooling, the oxygen is liberated and causes the characteristic "spitting." In malleability and ductility it is inferior only to gold, but as a conductor of heat and electricity it is superior to all other metals. The annual production of silver amounts to more than 250 million Troy ounces, about 40 per cent of the world's supply coming from Mexico. The metal was known in very ancient times.

The proper solvent for silver is nitric acid. It is insoluble in dilute hydrochloric and sulfuric acids, but dissolves readily in boiling sulfuric acid, with evolution of sulfur dioxide:

$$2\,Ag + 2\,H_2SO_4 \rightarrow 2\,H_2O + SO_2\uparrow + Ag_2SO_4$$

The solubility of silver in concentrated sulfuric acid is utilized in separating silver from gold and platinum in alloys.

Silver forms three oxides: silver suboxide, Ag_4O; silver oxide, Ag_2O; silver peroxide, Ag_2O_2. Of these oxides, Ag_2O alone is a basic anhydride; only one series of salts is known.

Silver peroxide is formed at the anode during the electrolysis of a concentrated, aqueous solution of silver nitrate. The grayish black crystalline powder has the composition: $Ag_4O_4 = Ag_2O \cdot Ag_2O_2$. It can be regarded as the silver salt of the hypothetical argentic acid, $HAgO_2$, and written $Ag[AgO_2]$.

Silver oxide, Ag_2O, is a brownish black powder, which on being heated to 300° is completely decomposed into metal and oxygen.

Most silver salts are colorless; the following, however, are colored: the bromide (pale yellow), the iodide (yellow), the sulfide (black), the phosphate (yellow), the arsenite (yellow), the arsenate (brown), the ferricyanide (orange), and the chromate (reddish brown). Most of the salts are insoluble in water, and are blackened on exposure to light. Silver tarnishes quickly in air containing hydrogen sulfide, and silver tableware blackens from contact with eggs, which contain sulfur. The readiness with which silver sulfide is formed is utilized in the hepar test for sulfur. The nitrate, chlorate, perchlorate, fluoride, nitrite, sulfate, and acetate are soluble in hot water.

Reactions in the Wet Way

1. **Hydrochloric Acid** or **Soluble Chlorides** precipitate white, curdy silver chloride from neutral and acid solutions:

$$Ag^+ + Cl^- \rightarrow \mathbf{AgCl}$$

Silver chloride is appreciably soluble in pure water (cf. p. 19), particularly on boiling, but it is quite insoluble if an excess of silver nitrate or a *slight* excess of hydrochloric acid is present (cf. p. 49).

Silver chloride dissolves to a considerable extent in a large excess of hydrochloric acid or of alkali chloride, owing to the formation of complex anions, $[AgCl_3^{--}]$, but it is much less soluble in dilute nitric acid.

It is very soluble in ammonia:

$$\mathbf{AgCl} + 2\ \mathbf{NH_3} \rightarrow [Ag(NH_3)_2]^+ + Cl^-$$

but is reprecipitated on addition of nitric acid to this solution:

$$[Ag(NH_3)_2]^+ + 2\ H^+ + Cl^- \rightarrow 2\ NH_4^+ + \mathbf{AgCl}$$

Silver chloride is also readily soluble in potassium cyanide solution:

$$\mathbf{AgCl} + 2\ CN^- \rightarrow [Ag(CN)_2]^- + Cl^-$$

and if such a solution is acidified, silver cyanide will be precipitated:

$$[Ag(CN)_2]^- + H^+ \rightarrow HCN + \mathbf{AgCN}$$

In the absence of acid, silver chloride is also readily soluble in a solution of sodium thiosulfate:

$$2\ \mathbf{AgCl} + 3\ S_2O_3^{--} \rightarrow [Ag_2(S_2O_3)_3]^{---} + 2\ Cl^-$$

On boiling this solution, silver sulfide is precipitated slowly if considerable $Na_2S_2O_3$ is present, but more quickly upon diluting.

It is evident that the solubility in all the above reactions is due to the formation of complex ions containing silver (cf. p. 27).

Silver chloride is slowly attacked by boiling, concentrated sulfuric acid, with evolution of hydrochloric acid and the formation of crystalline silver sulfate, insoluble in sulfuric acid.

By boiling with caustic soda or caustic potash solution, silver chloride is only partially decomposed; in the cold it is unaffected. Sodium carbonate solution does not affect it; but by fusing with sodium carbonate it is completely decomposed:

$$4\,AgCl + 2\,Na_2CO_3 \rightarrow 4\,NaCl + 2\,CO_2\uparrow + O_2\uparrow + 4\,Ag$$

By fusing silver chloride a yellow liquid is obtained, which on cooling solidifies to a vitreous mass; it may be removed from the crucible by treatment with zinc and dilute sulfuric acid (see p. 104).

2. **Alkali Hydroxides** precipitate brown silver oxide,

$$2\,Ag^+ + 2\,OH^- \rightarrow H_2O + \mathbf{Ag_2O}$$

insoluble in an excess of the precipitant, but readily soluble in nitric acid and in ammonia. If the solution in ammonia is allowed to stand, black fulminating silver (chiefly AgN_3) is deposited.

3. **Ammonia.** — If a neutral solution of a silver salt is cautiously treated with ammonia, the first drops produce a white precipitate, AgOH, which changes quickly to the brown oxide, Ag_2O. The greater part of the silver, however, remains in solution as complex silverdiammine salt; even the oxide is dissolved by an excess of ammonia:

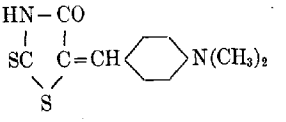
$$\mathbf{Ag_2O} + 4\,NH_3 + H_2O \rightarrow 2\,[Ag(NH_3)_2]^+ + 2\,OH^-$$

4. **Ammonium Carbonate** produces the same precipitate, but it is soluble in an excess of this reagent; $Ag(NH_3)_2^+$ ions are formed.

5. **Ammonium Thioacetate** also precipitates silver sulfide from acid solutions:

$$2\,Ag^+ + C_2H_3OS^- + H_2O \rightarrow \mathbf{Ag_2S} + HC_2H_3O_2 + H^+$$

6. ***p*-Dimethylaminobenzilidenerhodanine,**



(cf. p. 121), forms a red-violet salt with silver ions. Mercury, gold, platinum, palladium, and cuprous salts interfere.

In the absence of these elements, moisten a piece of filter paper with a saturated solution of the reagent in acetone and place on the dried paper 1 drop of the solution to be tested. If 0.02 γ of silver is present a red-violet precipitate, or spot, results which is easily distinguishable from the yellow-brown color of the reagent.

If mercury and copper are present add to the spot a few drops of dilute hydrochloric acid or ammonium chloride; this dissolves the mercury compound to form un-

dissociated $HgCl_2$ but does not affect the silver test as the organic salt is less soluble than AgCl.

If gold, platinum, and palladium are present, mix, on the spot plate, 1 drop of the solution to be tested, 1 drop of 10 per cent potassium cyanide solution, and 1 drop of the reagent dissolved in acetone. Stir and make acid with dilute nitric acid; if 2.5 γ of silver are present a pink coloration is obtained.

7. **Dithizone,** $SC\begin{matrix}/NH\cdot NHC_6H_5\\ \backslash N=NC_6H_5\end{matrix}$, gives a violet precipitate.

Place a drop of the neutral or slightly alkaline solution to be tested in a 3-ml test tube, add 1 drop of a solution obtained by dissolving 1–2 mg of dithizone in 100 ml of carbon tetrachloride, and shake; if 0.3 γ of silver is present a fine, violet precipitate will form and be distributed through the carbon tetrachloride. The test fails in the presence of noble metals and mercury, which also give precipitates; it succeeds in the presence of lead, zinc, and antimony if the test is carried out in an alkaline solution containing tartrate.

8. **Ferrous Sulfate** precipitates gray metallic silver from boiling solutions:

$$Ag^+ + Fe^{++} \rightarrow Fe^{+++} + Ag$$

Frequently a basic ferric salt is precipitated at the same time, particularly from very dilute solutions.

Ferrous sulfate added to an ammoniacal tartrate solution of a silver salt also causes the formation of a gray precipitate which may be silver suboxide, Ag_4O, or a mixture of finely divided silver with some organic substance.

9. **Formic acid,** $HCHO_2$, reduces silver solutions slowly:

$$2\,Ag^+ + HCHO_2 \rightarrow 2\,Ag + 2\,H^+ + CO_2\uparrow$$

10. **Hydrogen Sulfide** precipitates from neutral, ammoniacal, and acid solutions black silver sulfide:

$$2\,Ag^+ + H_2S \rightarrow 2\,H^+ + Ag_2S$$

insoluble in ammonia, alkali sulfides, and dilute potassium cyanide solution. Silver sulfide is so insoluble (cf. p. 22) that enough Ag^+ ions are present in aqueous solutions containing $[Ag(NH_3)_2]^+$ or even $[Ag(CN)_2]^-$ to exceed the solubility product of Ag_2S when in contact with slightly ionized hydrogen sulfide. Silver sulfide is, however, perceptibly soluble in a concentrated solution of potassium cyanide, and easily soluble in hot dilute nitric acid:

$$3\,Ag_2S + 2\,NO_3^- + 8\,H^+ \rightarrow 6\,Ag^+ + 2\,NO\uparrow + 4\,H_2O + 3\,S$$

11. **Potassium Chromate** precipitates brownish red silver chromate soluble in ammonia and in nitric acid:

$$2\,Ag^+ + CrO_4^{--} \rightarrow Ag_2CrO_4$$

12. **Potassium Dichromate** precipitates reddish brown silver dichromate soluble in ammonia and in nitric acid:

$$2\,Ag^+ + Cr_2O_7^{--} \rightarrow Ag_2Cr_2O_7$$

This test is sensitive and when carried out as a spot test will show 2 γ of silver.

Place a little of the solution to be tested on a watch glass, mix with an equal volume of ammonium carbonate solution, and filter off any precipitate that may form. To 1 drop of the clear filtrate on filter paper add 1 drop of 1 per cent potassium chromate solution which is normal in acetic acid.

13. **Potassium Iodide** precipitates yellow, curdy silver iodide, practically insoluble in ammonia, but easily soluble in potassium cyanide and sodium thiosulfate solutions.

The $[Ag(NH_3)_2]^+$ cation furnishes more Ag^+ cations than silver iodide in contact with water, but the $[Ag(CN)_2]^-$ and $[Ag_2(S_2O_3)_3]^{---}$ are much more stable complexes and furnish less Ag^+ cations than silver iodide does.

14. **Sodium Carbonate** precipitates white silver carbonate, which becomes yellow on being boiled; it is partially decomposed into oxide with loss of carbon dioxide:

$$2\,Ag^+ + CO_3^{--} \rightarrow Ag_2CO_3$$

$$Ag_2CO_3 \rightarrow Ag_2O + CO_2\uparrow$$

15. **Sodium Phosphate** throws down in neutral silver solutions a yellow precipitate of silver phosphate:

$$3\,Ag^+ + 2\,HPO_4^{--} \rightarrow H_2PO_4^- + Ag_3PO_4$$

Silver phosphate is easily soluble in nitric acid and in ammonia. The solubility of the phosphate in ammonia is due to the formation of complex silverdiammine ions:

$$Ag_3PO_4 + 6\,NH_3 \rightarrow 3\,[Ag(NH_3)_2]^+ + PO_4^{---}$$

By neutralizing the ammoniacal solution with nitric acid, or the nitric acid solution with ammonia, the silver phosphate is reprecipitated.

16. **Sodium Thiosulfate** precipitates white silver thiosulfate soluble in an excess of the reagent, but from the boiling solution silver sulfide is precipitated:

$$2\,Ag^+ + S_2O_3^{--} \rightarrow Ag_2S_2O_3$$

$$Ag_2S_2O_3 + 2\,S_2O_3^{--} \rightarrow [Ag_2(S_2O_3)_3]^{---}$$

$$[Ag_2(S_2O_3)_3]^{---} + 2\,H^+ \rightarrow Ag_2S + 2\,S + H_2O + SO_4^{--} + 2\,SO_2\uparrow$$

The presence of a little acid favors the precipitation of the sulfide in accordance with the last reaction.

17. **Stannous Chloride** precipitates silver from ammoniacal solutions:

$$Sn^{++} + 2\,Ag(NH_3)_2^+ \rightarrow Sn^{++++} + 2\,Ag + 2\,NH_3$$

Mix a little of the solution to be tested with an excess of ammonia and filter off any precipitate that forms. Place 1 drop of the clear filtrate on filter paper and add 1 drop of dilute stannous chloride solution. A black spot will form if 0.1 γ of silver is present. The treatment with ammonia removes bismuth and mercury, which would interfere.

18. **Zinc,** which is higher in the potential series than silver, precipitates it from neutral solutions. Similarly, if insoluble silver chloride is covered with dilute sulfuric acid and a piece of zinc placed in contact with the chloride, the chloride will be reduced to metal:

$$2\,AgCl + Zn \rightarrow Zn^{++} + 2\,Cl^- + 2\,Ag$$

Reactions in the Dry Way

Fused with soda on charcoal, all silver compounds yield a white, malleable, metallic button without incrustation (difference from lead and tin), readily soluble in nitric acid (difference from tin). The solution does not give a precipitate with very dilute sulfuric acid, but a precipitate forms immediately with hydrochloric acid (difference from lead).

MERCURY, Hg. At. Wt. 200.6, At. No. 80

Density 13.6. M. P. −38.9°. B. P. 357°

Occurrence. — Mercury occurs in nature chiefly in the form of rhombohedral cinnabar, HgS; from the ore, free mercury is obtained by distillation. Cinnabar is probably deposited in nature from solutions of its thio salt. The richest deposits are those of New Almaden in California, where it occurs with serpentine, Almaden in Spain, Idria in Carniola, and Moschellandsberg in the Palatinate of the Rhine. With cinnabar small quantities of native mercury are often found. Mercury is also an important constituent of many varieties of tetrahedrite.

Properties. — Mercury is the only metal that is liquid at ordinary temperatures, though the rare element gallium melts at 29.8°. It is named after the planet Mercury, and the symbol, Hg, is derived from the Latin *hydrargyrum* = water silver. Mercury has been known for a long time and the Almaden mine in Spain, which furnishes nearly half of the world's supply, has been worked continuously for more than 2500 years. The world's demand for mercury amounts to about 5700 tons a year. Mercury has a bright, silvery luster and is commonly called *quicksilver*. When precipitated from solutions in a finely divided state and when slightly impure, it forms a dark gray powder (sick mercury). It is not oxidized by air or oxygen at ordinary temperatures but oxidizes slowly at its boiling point. It dissolves many metals, forming amalgams which are of industrial importance. Amalgams are often formed by electrolysis of solutions with a mercury cathode. Mercury is insoluble in hydrochloric and dilute sulfuric acids, but it is soluble in hot concentrated sulfuric

acid with evolution of sulfur dioxide, forming mercurous or mercuric sulfate according to whether the metal or the acid is present in excess:

$$Hg + 2\,H_2SO_4 \rightarrow HgSO_4 + 2\,H_2O + SO_2\uparrow$$
$$2\,Hg + 2\,H_2SO_4 \rightarrow Hg_2SO_4 + 2\,H_2O + SO_2\uparrow$$

Hydrobromic acid hardly attacks the metal at all, but hydriodic acid dissolves it readily with evolution of hydrogen:

$$Hg + 4\,HI \rightarrow H_2[HgI_4] + H_2\uparrow$$

The position of mercury in the electromotive series (p. 43) shows that it cannot be oxidized by H^+ except when the concentration of Hg^{++} is extremely low. This explains why mercury does not dissolve in dilute hydrochloric or sulfuric acid. It seems remarkable, therefore, that mercury should be oxidized by hydriodic acid. The reason the hydrogen of hydriodic acid can accomplish the oxidation of the mercury is that the compound $H_2[HgI_4]$ is scarcely dissociated at all into Hg^{++} ions (cf. p. 29).

The proper solvent for mercury is nitric acid.

If the metal is treated with hot, concentrated nitric acid, mercuric nitrate is formed:

$$Hg + 4\,HNO_3 \rightarrow Hg(NO_3)_2 + 2\,H_2O + 2\,NO_2\uparrow$$

If, however, cold nitric acid is allowed to act upon an excess of mercury in the cold, mercurous nitrate is obtained:

$$Hg(NO_3)_2 + Hg \rightarrow Hg_2(NO_3)_2:$$

Mercury is attacked by chlorine, forming calomel (mercurous chloride):

$$2\,Hg + Cl_2 \rightarrow Hg_2Cl_2$$

Three oxides of mercury are known: black mercurous oxide, Hg_2O; yellow or red mercuric oxide, HgO; and reddish brown mercury peroxide, HgO_2. Mercurous oxide is formed by adding alkali hydroxide to the aqueous solution of a mercurous salt. It is not very stable and decomposes into mercury and HgO or into mercury and oxygen according to the conditions. Mercuric oxide is made on a large scale by heating mercurous nitrate until no more fumes of NO_2 are evolved. When made in this way, it is a bright red product. Yellow mercuric oxide, which is probably in a finer state of division, can be made by adding alkali hydroxide to a solution of a mercuric salt. On heating mercuric oxide it becomes vermilion in color, then black, and finally decomposes into mercury and oxygen. The undecomposed oxide regains its original color on cooling. Mercuric peroxide, HgO_2, has been prepared by adding concentrated hydrogen peroxide solution (perhydrol) to mercuric nitrate at 0°. It is fairly stable in air but decomposes slowly when in contact with water. There is doubt as to whether mercury forms any hydroxides.

The oxides HgO and Hg_2O are basic anhydrides, from which two series of salts are derived: (*a*) the mercuric salts, which contain Hg^{++}, and (*b*) the mercurous salts, which contain the group Hg_2^{++}. The reactions of mercurous compounds will be described here; the reactions of mercuric salts will be described under Group II.

Mercurous Salts

All mercurous salts contain the bivalent mercurous group Hg_2^{++} and are changed more or less readily into mercuric salts by splitting off one atom of mercury from the molecule. Mercurous salts containing oxygen are readily hydrolyzed, in dilute

aqueous solutions; thus the nitrate is decomposed according to the equation

$$Hg_2(NO_3)_2 + HOH \rightarrow HNO_3 + Hg_2(OH)NO_3$$

Mercurous chloride (calomel) is insoluble in water and hydrochloric acid, but soluble in nitric acid and aqua regia.

Reactions in the Wet Way

1. **Hydrochloric Acid** and **Soluble Chlorides** precipitate white mercurous chloride (calomel):

$$Hg_2(NO_3)_2 + 2\,Cl^- \rightarrow 2\,NO_3^- + Hg_2Cl_2$$

Contact with ammonia water causes the precipitate to turn black, owing to the formation of white mercuric amino-chloride (sometimes called *infusible precipitate*) and black, finely divided mercury:

$$Hg_2Cl_2 + 2\,NH_3 \rightarrow NH_4^+ + Cl^- + Hg(NH_2)Cl + Hg$$

By boiling the black precipitate with dilute HCl or concentrated NH_4Cl, $Hg(NH_2)Cl$ is dissolved and drops of mercury are left. Hg_2Cl_2 is insoluble in water and dilute acids, soluble in strong nitric acid and aqua regia. On boiling for a long time with water, calomel becomes gray, owing to a partial decomposition into mercuric chloride and mercury. On boiling with concentrated sulfuric acid, mercuric sulfate is formed with evolution of sulfur dioxide and hydrogen chloride:

$$(a)\ Hg_2Cl_2 + H_2SO_4 \rightarrow 2\,HCl\uparrow + Hg_2SO_4$$

$$(b)\ Hg_2SO_4 + 2\,H_2SO_4 \rightarrow 2\,H_2O + SO_2\uparrow + 2\,HgSO_4$$

2. **Alkali Carbonates** give, first, a yellow precipitation of the carbonate, which quickly becomes gray, owing to the formation of mercuric oxide and metallic mercury with evolution of carbon dioxide:

$$Hg_2(NO_3)_2 + Na_2CO_3 \rightarrow 2\,NaNO_3 + Hg_2CO_3$$

and

$$Hg_2CO_3 \rightarrow HgO + Hg + CO_2\uparrow$$

3. **Alkali Hydroxides** precipitate black mercurous oxide:

$$Hg_2(NO_3)_2 + 2\,OH^- \rightarrow 2\,NO_3^- + H_2O + Hg_2O$$

4. **Ammonia** or $(NH_4)_2CO_3$ solution produces a black precipitate of mercuric amino salt mixed with metallic mercury:

$$2\,Hg_2(NO_3)_2 + 4\,NH_3 + H_2O \rightarrow 3\,NH_4NO_3 + O\begin{matrix}\diagup\,Hg\,\diagdown\\ \diagdown\,Hg\,\diagup\end{matrix}NH_2NO_3 + 2\,Hg$$

It can easily be shown that this precipitate contains metallic mercury by rubbing a piece of pure gold over it; silver-lustrous gold amalgam will be formed. See §1 for reaction of Hg_2Cl_2 and NH_3.

5. **Ammonium Thioacetate** and **Sodium Thiosulfate** produce sulfide precipitates when added to acid solutions of mercurous salts, the

precipitates consisting of black mercuric sulfide and finely divided mercury together with sulfur.

6. **Polished Copper** touched with a drop of nearly neutral mercurous solution causes the deposition of metallic mercury. If, after a short time, the solution is washed off and the copper is rubbed gently with a woolen cloth or piece of paper, a silver-white, lustrous spot is obtained.

7. **Hydrogen Sulfide** immediately throws down a black precipitate of mercuric sulfide and mercury (difference from mercuric salts):

$$Hg_2^{++} + H_2S \rightarrow \mathbf{HgS} + \mathbf{Hg} + 2\,H^+$$

The black precipitate does not dissolve completely in potassium sulfide, the mercury remaining insoluble, but in alkali polysulfides the entire precipitate dissolves.

From such a solution, ammonium chloride throws down black mercuric sulfide.

8. **Neutral Potassium Chromate** precipitates red mercurous chromate on boiling (cf. p. 204):

$$Hg_2(NO_3)_2 + K_2CrO_4 \rightarrow 2\,KNO_3 + \mathbf{Hg_2CrO_4}$$

9. **Potassium Cyanide** precipitates metallic mercury, mercuric cyanide being formed at the same time:

$$Hg_2(NO_3)_2 + 2\,KCN \rightarrow 2\,KNO_3 + \mathbf{Hg(CN)_2} + \mathbf{Hg}$$

10. **Potassium Iodide** precipitates green mercurous iodide,

$$Hg_2(NO_3)_2 + 2\,KI \rightarrow 2\,KNO_3 + \mathbf{Hg_2I_2}$$

partly soluble in an excess of the precipitant, with the formation of potassium mercuric iodide and the separation of mercury:

$$\mathbf{Hg_2I_2} + 2\,I^- \rightarrow [HgI_4]^{--} + \mathbf{Hg}$$

11. **Stannous Chloride** added in very small quantities precipitates white mercurous chloride, but if more than an equivalent weight of stannous ions is added, a gray mixture of mercurous chloride and finely divided mercury is obtained, and eventually all the mercurous chloride can be changed to free mercury:

$$Hg_2(NO_3)_2 + Sn^{++} \rightarrow Sn^{++++} + 2\,NO_3^- + 2\,\mathbf{Hg}$$

Reactions in the Dry Way

Nearly all mercury compounds sublime on being heated in the closed tube. Mercuric chloride first melts, then vaporizes, forming a crystalline deposit on the cold sides of the tube. Mercurous chloride sublimes; the sublimate is almost white, but there is a slight grayish

tint owing to the decomposition of a small part of the substance into mercuric chloride and mercury. Mercuric iodide yields a yellow sublimate, which becomes red on being rubbed with a glass rod. The sulfide gives a black sublimate. Mercury compounds containing oxygen (all more or less unstable) yield mercury.

All compounds of mercury, when mixed with sodium carbonate and heated in a closed tube, yield a gray mirror, consisting of small globules of mercury. In order to make the drops more apparent, place a piece of filter paper over a glass rod, and rub the mirror with it. The small drops then run together into large ones, stick to the paper, and can be removed from the glass.

SPECIAL PROCEDURES FOR MERCURY

*Detection of Mercury in Urine**

Treat 500 to 1000 ml of urine in a beaker with 0.5 per cent hydrochloric or sulfuric acid, add 0.5 g of brass wool (such as is used for the ornamentation of Christmas trees) and, while heating on the water-bath to 60°–80°, pass air through the liquid for ten to fifteen minutes, to keep it in constant motion. Any mercury present is replaced by copper: $HgCl_2 + Cu \rightarrow CuCl_2 + Hg$.

The mercury, as fast as it is set free, amalgamates with the excess of copper present. Pour off the liquid from the tiny threads of brass and wash thoroughly by decantation with distilled water, then with alcohol, and finally with ether. Press the brass threads between layers of filter paper, to free them from any adhering ether, and roll them between the fingers into a small pellet. Introduce this pellet into a thoroughly cleansed and perfectly dry glass tube, 10 cm long, 0.5 cm wide, and closed at one end. With the aid of the blast flame, draw out a capillary of about 1 mm width in the tube about 0.5 cm away from the brass, toward the open end of the tube. After cooling the tube, heat the bottom of it, in which the sample rests, to dark redness. This causes the mercury to distil off, and it is condensed in the colder portion of the tube in a gray mirror consisting of tiny drops. If any considerable amount of mercury is present, *e.g.*, more than 1 mg, the drops of mercury can be distinctly seen with a lens. If less than 1 mg of mercury is present in the urine, it is very difficult to distinguish the mirror. In this case, to make it perceptible, transform the mercury into scarlet-red mercuric iodide. To accomplish this, place a small crystal or two of iodine in a test tube and cut off the tube containing the mercury mirror just above the place where the ball of brass rests and place the part of the tube containing the mercury in the test tube. Cautiously heat the bottom of the test tube over a gas flame. As soon as the violet vapors of iodine reach the place where the mercury was deposited, the latter is transformed, by very gentle heating, into the red iodide, which can be seen most distinctly by removing the little tube and laying it upon a piece of white paper. This method is very sensitive and permits the positive recognition of as little as 0.4 mg of $HgCl_2$.†

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* P. Fübringer, *Z. anal. Chem.*, **27**, 526 (1888).

† For other methods of detecting mercury in urine, see Jolles, *Z. anal. Chem.*, **39**, 230 (1900); Merget, *J. pharm. chim.* [5], **19**, 444 (1889); and Oppenheim, *Z. anal. Chem.*, **42**, 431 (1903).

Detection of Mercury Vapors in the Air

Place a piece of pure gold leaf in a small glass tube and draw the air to be tested through the tube for an hour, at a rate not greater than one liter per minute. Meanwhile evacuate a Geissler tube, of the form shown in Fig. 11, by means of a water pump (not a mercury pump!) and finally close both stopcocks. Place the gold leaf, which now contains as amalgam any mercury that was present in the air tested, in the tube *n* and suddenly open the cock *a*, which has a wide bore; this causes the gold to be sucked into the tube, stopping at *c*, the mouth of the capillary opening. The next step is to replace the air in the tube by hydrogen. Introduce hydrogen gas, obtained from a Kipp generator and dried by concentrated sulfuric acid, at *a* and allow the gas to pass out at *b*. After a rapid stream of the gas has passed through the tube for three minutes, close the cocks *a* and *b*, without disconnecting the Kipp generator, connect *b* with the suction pump,* and evacuate the apparatus for a minute or two; then close *b* and open *a* (which causes more hydrogen to enter the apparatus); close *a* again, open *b*, and once more evacuate the apparatus. Repeat this alternate introduction of hydrogen gas and evacuation five or six times. In this way the air is entirely replaced by hydrogen. Finally evacuate the tube for five or ten minutes and close the cock *b*. Place the capillary in front of the slit of a spectroscope and allow the secondary current of an induction apparatus to pass through the tube. In the presence of the merest trace of mercury, the characteristic green line 546 $m\mu$ is distinctly visible in the cold, and with somewhat larger amounts of mercury the indigo-blue line at 456 $m\mu$ can be seen. If the wad of gold leaf is cautiously warmed with the Bunsen flame, the mercury spectrum appears still more sharply.

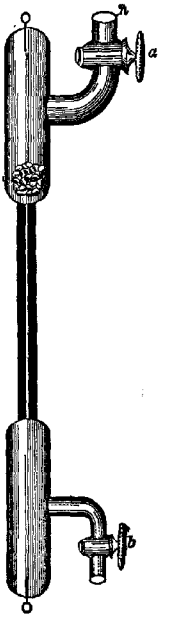


FIG. 11

Remark. This test is so extremely sensitive that a blank test performed in places where work with mercury has been performed will often show the presence of this element in the atmosphere.

If the apparatus has been once used for the detection of mercury it must be thoroughly cleansed before it is used again for this purpose. To this end, remove the gold and allow aqua regia to remain in the tube for several minutes. Draw out the acid and rinse the tube three times with distilled water and once with absolute alcohol;† finally dry by passing dry hydrogen through the tube for five minutes, while warming it at the same time. Ignite the gold gently to distil off any mercury it may contain. If now on introducing the gold and evacuating the apparatus, the mercury spectrum is no longer visible, the tube is ready for a new experiment.

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* Between the water suction-pump and the Geissler tube, a calcium chloride drying tube should be introduced.

† All these operations must be carried out in a space where there are positively no mercury vapors present in the atmosphere.

It may be mentioned that the two platinum wires in the Geissler tube must not be provided with aluminum points, because aluminum amalgamates with mercury, and when the points are once amalgamated it is impossible to free the tube sufficiently from mercury to permit its use for subsequent experiments.

LEAD, Pb. At. Wt. 207.21, At. No. 82

Density 11.38–11.48. M. P. 327.4°. B. P. 1613°

Occurrence. — Galena, PbS, isometric; cerussite, $PbCO_3$, orthorhombic and isomorphous with aragonite, $CaCO_3$; anglesite, $PbSO_4$, orthorhombic, isomorphous with anhydrite, $CaSO_4$, celestite, $SrSO_4$, and barite, $BaSO_4$; pyromorphite, $Pb_5(PO_4)_3Cl$, hexagonal; mimetite, $Pb_5(AsO_4)_3Cl$; vanadinite, $Pb_5(VO_4)_3Cl$. The last three minerals are isomorphous and belong to the apatite group. Other minerals which may be mentioned are wulfenite, $PbMoO_4$, tetragonal, isomorphous with stolzite, $PbWO_4$, and the monoclinic crocoite, $PbCrO_4$.

Properties. — Lead, which owes its English name to the Anglo-Saxon *lead* and its symbol to the Latin word *plumbum*, is a soft, malleable, slightly ductile, bluish gray metal which tarnishes in the air to form a protective film of oxide. Very small quantities of other metals harden it. It is a poor conductor of electricity and heat. Lead boils before the oxyhydrogen blowpipe but cannot be distilled like zinc or cadmium by heating in a closed vessel. In the absence of air, lead is not appreciably volatile below a white heat. Lead forms many useful alloys such as Babbitt metal, type metal, solder, pewter, shot metal, and fusible metals. About 1,300,000 tons of lead are produced annually.

Lead is attacked by all acids. As, however, most lead salts are difficultly soluble in water, the metal usually becomes coated with a layer of salt, which protects it from further action of the acid. Thus lead is immediately attacked by dilute sulfuric acid according to the equation

$$Pb + H_2SO_4 \rightarrow PbSO_4 + H_2 \uparrow$$

But, since lead sulfate is insoluble in dilute sulfuric acid, the reaction quickly ceases. Upon this principle rests the use of "lead chambers" in the manufacture of sulfuric acid, and the use of "lead pans" for the concentration of the dilute "chamber acid." It has been found from experience, however, that the sulfuric acid should not be concentrated too much in lead pans — stopping when a 78–82 per cent acid is obtained. The protecting layer of lead sulfate is soluble in hot concentrated sulfuric acid, forming soluble lead bisulfate, $PbSO_4 + H_2SO_4 \rightarrow Pb(HSO_4)_2$, so that the hot concentrated acid can act on the freshly exposed surface of lead:

$$Pb + 3\,H_2SO_4 \rightarrow 2\,H_2O + Pb(HSO_4)_2 + SO_2 \uparrow$$

Lead behaves quite similarly on treatment with hydrochloric acid. On the surface a protecting coating of lead chloride is obtained, which is soluble in hot concentrated hydrochloric acid, forming $H[PbCl_3]$. Lead is soluble, therefore, in concentrated hydrochloric acid:

$$Pb + 3\,HCl \rightarrow H[PbCl_3] + H_2 \uparrow$$

Hydrofluoric acid attacks lead similarly, forming a protecting layer of lead fluoride, which is insoluble in hydrofluoric acid. Consequently lead retorts can be used for the distillation of hydrofluoric acid and in the preparation of hydrofluoric acid by means of fluorite and sulfuric acid.

Dilute nitric acid is the proper solvent for lead. Lead nitrate is insoluble in strong nitric acid, so that lead does not dissolve in concentrated nitric acid; the solution must be sufficiently dilute to prevent the deposition of the lead nitrate formed.

Six oxides of lead have been described: Pb_2O, PbO, $Pb_3O_7 \cdot 3\,H_2O$, Pb_2O_3, Pb_3O_4, and PbO_2. Lead suboxide, Pb_2O, is the black powder obtained by heating lead oxalate, PbC_2O_4, below 300° out of contact with air. It is unstable and changes into Pb and PbO so readily that some chemists have doubted its existence. Lead monoxide, PbO, exists in two modifications — yellow litharge and red massicot. This oxide is formed by heating Pb, PbO_2, Pb_3O_4, $Pb(OH)_2$, $PbCO_3$, PbC_2O_4, or $Pb(NO_3)_2$ in the air; the color of the product is determined largely by the temperature reached, high temperature forming the yellow compound. According to the old nomenclature, PbO is *lead protoxide*. Lead sesquioxide, or dileadtrioxide, Pb_2O_3, is obtained as a yellow precipitate by *gently* oxidizing an alkaline solution of lead monoxide with alkali hypochlorite, halogen, hydrogen peroxide, or alkali persulfate:

$$2\,PbO_2^{--} + H_2O + Cl_2 \rightarrow \mathbf{Pb_2O_3} + 2\,Cl^- + 2\,OH^-$$

Pb_2O_3 can be regarded as lead metaplumbate (see below).

Trileadtetroxide, Pb_3O_4, is usually called *red lead* or *minium*. It is a bright red powder formed by long heating of litharge at 400°, with frequent stirring to insure contact with the oxygen of air. At higher temperatures it decomposes with liberation of oxygen. Pb_3O_4 can be regarded as lead orthoplumbate (see below).

Both Pb_2O_3 and Pb_3O_4 behave chemically as salts, for, on treating with nitric acid, brown plumbic acid and lead nitrate are formed, which corresponds to the action of nitric acid, on say, lead carbonate:

$$\mathbf{PbPbO_3} + 2\,H^+ \rightarrow Pb^{++} + \mathbf{H_2PbO_3}$$

$$\mathbf{Pb_2PbO_4} + 4\,H^+ \rightarrow 2\,Pb^{++} + H_2O + \mathbf{H_2PbO_3}$$

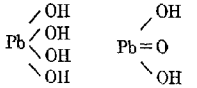
These salt-like oxides are perfectly analogous to those of manganese; on treatment with hydrochloric acid they yield chlorine, the plumbic acid, at first set free, behaving like a peroxide:

$$\mathbf{PbO_2} + 4\,HCl \rightarrow 2\,H_2O + PbCl_2 + Cl_2\uparrow$$

$$\mathbf{Pb_2O_3} + 6\,HCl \rightarrow 3\,H_2O + 2\,PbCl_2 + Cl_2\uparrow$$

$$\mathbf{Pb_3O_4} + 8\,HCl \rightarrow 4\,H_2O + 3\,PbCl_2 + Cl_2\uparrow$$

Lead dioxide is a dark brown powder which can be regarded as the anhydride of orthoplumbic acid, H_4PbO_4, or of metaplumbic acid, H_2PbO_3



Orthoplumbic acid Metaplumbic acid

just as SiO_2, SnO_2, CO_2, and MnO_2 are anhydrides of silicic, stannic, carbonic, and manganous acids. The acid H_2PbO_3 is formed by a stronger oxidation than is used to form Pb_2O_3, in alkaline solution with hypochlorites, chlorine, bromine, hydrogen peroxide, or potassium persulfate:

$$\mathbf{Pb(OH)_2} + 2\,OH^- + Cl_2 \rightarrow H_2O + 2\,Cl^- + \mathbf{H_2PbO_3}$$

The brown metaplumbic acid which separates out goes over at 100° C into the anhydride; and the latter on ignition loses oxygen, changing into yellow PbO.

Of these oxides, lead monoxide, PbO, is the only one of distinctly basic properties, and from it all common lead salts are derived. There are, to be sure, a number of

subsalts, such as PbCl, which have been prepared and in which lead is univalent. There are also some salts such as lead tetra-acetate, $Pb(C_2H_3O_2)_4$, in which lead is present as a quadrivalent cation, but these salts are unimportant and rarely encountered. Lead monoxide (litharge) melts at 980° and solidifies on slow cooling in tetragonal needles. It is somewhat amphoteric and forms plumbites as well as the common bivalent lead salts.

Besides the lead salts of plumbic acid, alkali and alkaline earth plumbates are known.

Reactions in the Wet Way

Most lead salts are difficultly soluble or insoluble in water; but all dissolve in dilute nitric acid, except, perhaps, fused lead chromate, which is very difficultly soluble.

1. **Hydrochloric Acid** or **Soluble Chlorides** precipitate from moderately concentrated solutions, white flocculent lead chloride:

$$Pb^{++} + 2\,Cl^- \rightarrow \mathbf{PbCl_2}$$

difficultly soluble in cold water (135 parts of water dissolve 1 part of $PbCl_2$), but much more soluble in hot water; on cooling the solution, lead chloride separates in the form of glistening needles or plates. Lead chloride is much more soluble in concentrated hydrochloric acid and in a concentrated solution of a chloride of an alkali than it is in water, since it forms complex compounds with these substances such as $H[PbCl_3]$, $K[PbCl_3]$, which are, however, decomposed on dilution with water, with separation of lead chloride.

2. **Alkali Hydroxides** precipitate white lead hydroxide:

$$Pb^{++} + 2\,OH^- \rightarrow \mathbf{Pb(OH)_2}$$

soluble in an excess of the precipitant, forming a plumbite:

$$\mathbf{Pb(OH)_2} + OH^- \rightarrow H_2O + HPbO_2^-$$

$Pb(OH)_2$ is also slightly soluble in water which is free from carbonic acid. The aqueous solution of lead hydroxide is slightly alkaline. The addition of hydrogen peroxide, hypochlorite, or persulfate causes precipitation of dark brown lead peroxide, PbO_2.

3. **Alkali Carbonates** precipitate white basic lead carbonate. *Alkali bicarbonates* precipitate the normal carbonate.

4. **Alkali Chromates** produce a yellow precipitate of lead chromate:

$$Pb^{++} + CrO_4^{--} \rightarrow \mathbf{PbCrO_4}$$

and

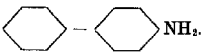
$$2\,Pb^{++} + Cr_2O_7^{--} + 2\,C_2H_3O_2^- + H_2O \rightarrow 2\,HC_2H_3O_2 + 2\,\mathbf{PbCrO_4}$$

Lead chromate is insoluble in acetic acid, but soluble in nitric acid and in caustic alkali.

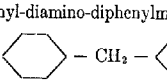
5. **Ammonia** precipitates the white hydroxide, insoluble in excess of the reagent.

6. **Ammonium Thioacetate** added to a hydrochloric acid solution of a lead salt produces at first a red precipitate of sulfochloride and finally a black precipitate of lead sulfide.

7. **Benzidine** and also **Arnold's Base** are oxidized to blue meriquinoidal products by lead dioxide, and either reaction can be used as a sensitive test for lead.

Benzidine is $C_{12}H_8(NH_2)_2$ or H_2N  NH_2.

Arnold's base is tetramethyl-diamino-diphenylmethane,

$(CH_3)_2N$  $N(CH_3)_2$

Procedure. — Moisten a piece of filter paper with an ammoniacal solution of 3 per cent hydrogen peroxide. Follow this with a drop of the solution to be tested, and hold the paper over steam or allow it to stand for a few minutes. This causes PbO_2 to form and makes the excess of hydrogen peroxide harmless. Finally add a drop of benzidine or Arnold's base solution in acetic acid. The test can be obtained with 1.5 γ of lead.

8. **Diphenylthiocarbazone** (dithizone) $SC\begin{matrix}\diagup NH \cdot NHC_6H_5 \\ \diagdown N=NC_6H_5\end{matrix}$ forms a brick-red complex compound with lead salts in neutral, ammoniacal, alkaline, and alkali cyanide solutions.

Place a drop of the solution to be tested in a small test tube, add a drop of dithizone reagent, and shake well. As little as 0.04 γ of lead will give the test in a neutral solution. The fact that the test is obtained in solutions containing potassium cyanide and alkali tartrate makes this a specific test for lead in the presence of other heavy metals. The test has been used a great deal for detecting lead in urine and in other biological fluids. As reagent a solution of 1–2 mg of dithizone in 100 ml of carbon tetrachloride is used.

9. **Hydrogen Sulfide** produces in dilute lead solutions (from slightly acid solutions, as well as from neutral or alkaline ones) a black precipitate of lead sulfide:

$$Pb^{++} + H_2S \rightleftarrows 2\,H^+ + \mathbf{PbS}$$

From hydrochloric acid solutions an orange-red precipitate of lead sulfochloride is at first obtained:

$$2\,PbCl_2 + H_2S \rightarrow 2\,HCl + Pb_2Cl_2S$$

which is decomposed immediately by more hydrogen sulfide, forming the black lead sulfide. In this respect lead salts are similar to mercuric salts (see p. 119).

Lead sulfide is soluble in dilute, boiling, 2-normal nitric acid, forming lead nitrate, with separation of sulfur:

$$3\,PbS + 2\,NO_3^- + 8\,H^+ \rightarrow 3\,Pb^{++} + 4\,H_2O + 2\,NO\uparrow + 3\,S$$

The reaction usually goes a little farther; some of the sulfur is oxidized to sulfuric acid, forming insoluble lead sulfate. The amount of sulfuric acid formed (and therefore of the lead sulfate also) increases with the concentration of the acid.

Lead sulfide is also soluble in strong hydrochloric acid:

$$PbS + 2\,H^+ \rightleftarrows Pb^{++} + H_2S\uparrow$$

10. **Potassium Cyanide** precipitates white lead cyanide, insoluble in an excess.

11. **Potassium Iodide** precipitates yellow lead iodide:

$$Pb^{++} + 2\,I^- \rightarrow \mathbf{PbI_2}$$

The iodide is much less soluble in water than the chloride (195 ml of boiling water dissolve only 1 g of lead iodide), forming a colorless solution from which lead iodide separates on cooling, in the form of golden yellow plates.

The iodide dissolves to a considerable extent in hydriodic acid, and in a solution of an alkali iodide, forming lead hydriodic acid, $H[PbI_3]$, or one of its salts (such as $K[PbI_3]$), all of which are decomposed on dilution, with deposition of lead iodide.

12. **Sodium Phosphate** precipitates white lead phosphate:

$$3\,Pb^{++} + 4\,HPO_4^{--} \rightarrow 2\,H_2PO_4^- + \mathbf{Pb_3(PO_4)_2}$$

insoluble in acetic acid, readily soluble in nitric acid, caustic soda, or potash.

13. **Sodium Thiosulfate** produces a white precipitate of lead thiosulfate, soluble in an excess of the precipitant, forming, as in the case of a silver salt, a complex thiosulfate ion. In the presence of acid, lead sulfide is precipitated on boiling.

14. **Stannous Chloride** and **Potassium Iodide** form with bivalent lead cations a deep orange-red complex salt, $2\,PbI_2 \cdot SnI_2$. Since lead sulfate responds to the test, this reaction is useful as a spot test for detecting lead in the presence of other metals.

The reagent should be freshly prepared as follows: To a solution made by dissolving tin in strong hydrochloric acid, add saturated potassium iodide solution until, upon shaking, the liquid solidifies to a pale yellow mass. Then add dropwise a saturated solution of cadmium nitrate until the pale yellow mass dissolves. The reagent is stable toward water, but yellow stannous iodide precipitates when sulfuric acid is added. In making the test, therefore, the presence of free sulfuric acid must be guarded against.

Procedure. — Place a drop of dilute sulfuric acid upon a piece of thick filter paper. When the liquid has been well absorbed by the paper, place a drop of the solution to be tested at the middle of the spot and add a drop more of dilute sulfuric acid to make sure that all the lead is transformed to sulfate, which will adhere to the filter paper. Moisten the test spot with water from a fine capillary tube and wash away any soluble salts. When this is accomplished, add a drop of the reagent to the middle of the spot, where the lead sulfate was deposited. If 10 γ of lead is present, a more or less intensive orange-red coloration will appear.

15. **Sulfuric Acid** and **Soluble Sulfates** in solutions of lead salts cause the separation of white, difficultly soluble lead sulfate:

$$Pb^{++} + H_2SO_4 \rightarrow 2\,H^+ + \mathbf{PbSO_4}$$

One gram of the salt dissolves at the ordinary temperature in 22,800 ml of water; in water containing a little sulfuric acid it is still less soluble, while in alcohol it is insoluble. Lead sulfate dissolves appreciably in hot, dilute hydrochloric or nitric acid, forming $Pb(HSO_4)_2$. On cooling the hydrochloric acid solution, lead chloride separates out in needles. Almost all the sulfuric acid of commerce contains some dissolved lead sulfate. In order to detect this, 200–300 ml of the concentrated acid

should be diluted with an equal volume of water and allowed to stand twelve hours, whereby the lead sulfate separates as a white powder.

Besides being soluble in acids, lead sulfate is easily soluble in caustic alkalies, and in solutions containing the ammonium salts of many organic acids. This last property is of great importance for the analytical chemist, as it offers a means for separating lead sulfate from barium sulfate, silica, etc., which remain undissolved. Ammonium acetate or ammonium tartrate is generally used as the solvent. A little lead sulfate usually remains undissolved when $BaSO_4$ is present.

The reason lead sulfate dissolves in a *concentrated* solution of ammonium acetate is that lead acetate forms, which is ionized only to a very slight extent in the presence of an excess of acetate ions:

$$PbSO_4 + 2\ C_2H_3O_2^- \rightarrow Pb(C_2H_3O_2)_2 + SO_4^{--}$$

Similarly, ammonium tartrate in aqueous solution dissolves lead sulfate by forming a tartrate which does not ionize to any extent into simple lead cations. Lead sulfate also dissolves easily in caustic alkali solutions, forming alkali plumbites.

From all these solutions made acid with acetic acid, the lead can be precipitated as chromate by the addition of potassium chromate, as sulfate upon the addition of dilute sulfuric acid, or as sulfide by ammonium sulfide.

Reactions in the Dry Way

Heated with sodium carbonate on charcoal, all lead compounds yield a malleable button, surrounded with an incrustation of the yellow oxide. On the charcoal stick, also, the malleable button is readily obtained.

Lead glass turns black on heating in the reducing flame, owing to the separation of lead.

ANALYSIS OF GROUP I

Silver, lead, and mercurous chlorides are difficultly soluble in water. According to the table on page 21, 0.038 mg Hg_2Cl_2, 0.15 mg $AgCl$, and about 1 g $PbCl_2$ will dissolve in 100 ml of water. From these values, it is evident that the precipitation of mercurous and silver cations will be nearly complete from 100 ml of solution and that, although lead chloride is much less soluble in a solution containing an excess of chloride ions than it is in water, lead will never be precipitated completely as chloride from aqueous solutions. By the addition of a large excess of alcohol, however, the precipitation of lead chloride can be made nearly complete, but the addition of alcohol at this stage of the analysis is rarely permissible except in the analysis of certain alloys or compounds rich in lead.

Lead chloride is characterized by the fact that it is much more soluble in hot water than in cold. On dissolving lead compounds in a small quantity of hydrochloric acid, the chloride often separates out as the solution cools, and it is easier to remove the lead chloride at this stage of the analysis than to precipitate it as sulfide, dissolve in nitric acid, and reprecipitate as sulfate.

As group precipitant either hydrochloric acid or ammonium chloride can be used. Any other soluble chloride would accomplish the same end but would interfere more with the subsequent analysis. If the solution is originally alkaline, the addition of hydrochloric acid may cause the formation of some other precipitate. Thus an

alkaline cyanide solution, a solution of thio salt in ammonium sulfide, and an alkaline silicate solution will often give precipitates upon the addition of any acid. Such precipitates may dissolve upon the addition of a little more acid and cause no trouble, but sometimes it is best to treat the precipitate as an insoluble substance by the methods described in Part IV.

Bismuth, antimony, and stannic chloride solutions on being diluted with water are changed into insoluble basic salts. These precipitates may be filtered off and dissolved by repeatedly passing a little 2-normal hydrochloric acid through the filter. Then, since the solution thus obtained is likely to contain lead chloride, if lead is present in the sample analyzed, it is best to evaporate to about 1 ml, dilute with 25 ml of water, and precipitate with hydrogen sulfide without paying any attention to the formation of a basic salt upon diluting: such basic salts are changed by hydrogen sulfide to less soluble sulfides.

TABLE I. — ANALYSIS OF THE SILVER GROUP

Solution may contain all the metals. *Add 6-normal HCl in slight excess, filter, and examine the filtrate for succeeding groups. Treat the precipitate with hot water.* (1)

Residue: AgCl, Hg_2Cl_2. *Pour ammonia through the filter.* (3)		Solution: Pb^{++}. *Test for lead with H_2SO_4. Filter off $PbSO_4$ and treat the precipitate with hot $NH_4C_2H_3O_2$ solution. Add K_2CrO_4; a yellow precipitate of $PbCrO_4$ shows presence of Pb.* (2)
Residue: Black $Hg(NH_2)Cl+Hg$.	Solution: $[Ag(NH_3)_2]^+$. *Add HNO_3: white precipitate shows the presence of Ag.* (4)	

The analysis of the first group of metals is based upon the solubility of lead chloride in hot water, the solubility of silver chloride in ammonia, and the blackening of mercurous chloride by ammonia.

PROCEDURE

1. To the cold, concentrated solution add 6-normal hydrochloric acid and, if a precipitate is formed, continue adding hydrochloric acid, drop by drop, until no further precipitation takes place. Filter through a small filter (cf. p. 70), and wash the precipitate four times with a little cold water, blowing a fine stream from the wash bottle around the upper edge of the filter and waiting each time until the filter has drained before adding a fresh portion of water. Do not use more than 5 ml of water each time. Take the entire filtrate for the analysis of Groups II, III, IV, and V. Pour a little hot water through the filter. Test the residue by (3).

2. Test the first 5-ml portion of hot water that runs through the filter for lead by adding a few drops of concentrated sulfuric acid. If a precipitate forms, filter, wash once with cold water, and then pour 10 ml of hot 3-normal ammonium acetate solution through the filter.

Add a few drops of potassium chromate solution to the solution and 3 ml of 6-normal acetic acid. A yellow precipitate of lead chromate should form if *lead is present.* Continue washing the chlorides with hot water until 5 ml of the washings will give no test for lead with potassium chromate solution.

3. Pour 5 ml of 6-normal ammonia around the upper edge of the filter, catching it, as it runs through the funnel, in a test tube. Acidify the filtrate with nitric acid. A white, curdy precipitate of silver chloride is formed when *silver is present.* The treatment with ammonia causes any mercurous chloride to turn black on the filter (cf. p. 106).

If considerable mercurous chloride and very little silver chloride is present, the treatment with ammonia may fail to dissolve silver chloride. In such a case, wash the black residue and pour repeatedly a mixture of 3 ml 6-normal hydrochloric acid and 10 ml of saturated bromine water through the filter. This serves to convert the mercurous chloride to soluble mercuric salt and leaves the silver on the filter as silver chloride or bromide. Wash the filter with hot water, and again pour 5 ml of ammonium hydroxide through it, and test the ammoniacal solution for silver with nitric acid.

Quiz Questions*

1. Give, in tabular form, an outline scheme for the anal. of a soln. contg. a mixt. of $Hg_2(NO_3)_2$, $AgNO_3$ and $Pb(NO_3)_2$. Write formulas of materials, reagents and products. State colors and soly.

2. The *Sp* of Ag_3PO_4 at room temp. is 1.8×10^{-18}. How many grams dissolve in 1 l of water? Ag = 108. P = 31. O = 16.

3. Write balanced reactions for

(*a*) action of NH_4OH soln. on AgCl ppt. (*b*) action of Br_2 and HCl on the black ppt. formed in the anal. of Group I. (*c*) action of NH_4OH soln. on Hg_2Cl_2.

4. Explain briefly by the *Sp* principle why Hg_2Cl_2 is less soluble in 2 *N* HCl than in water but more soluble in 6 *N* HCl than in water.

5. In making up 1 l of 6 *N* H_2SO_4 soln. how many milliliters of 96 per cent H_2SO_4 (*d.* 1.84) should be used?

6. If 0.11 g of $PbCl_2$ will just dissolve in 10 ml of water, calculate the *Sp* of lead chloride.

7. If Pb^{++} is present in a soln. to be analyzed, explain by the *Sp* principle why the presence of a moderate excess of NH_4Cl tends to keep more of the Pb in Group I and less in Group II.

8. Write equations expressing all the chemical reactions involved in the anal. of the silver group ppt.

9. What wt. of NH_4Cl is required to make 3 l of 0.5 *N* NH_4Cl soln.? How many milliliters of H_2SO_4 (*d.* 1.84 contg. 96 per cent H_2SO_4 by wt.) should be taken to make 2 l of 6 *N* acid?

10. If the *Sp* of $Ag_2Cr_2O_7$ is 2.0×10^{-7}, compute the wt. required to form 500 ml of satd. soln. contg. 0.170 g of $AgNO_3$.

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* These questions are taken from quizzes given at the Massachusetts Institute of Technology. Usually three questions were given at a time. The abbreviations are mostly those used in *Chemical Abstracts.*

GROUP II. HYDROGEN SULFIDE GROUP

MERCURY, LEAD, COPPER, BISMUTH, CADMIUM, ARSENIC, ANTIMONY, TIN (GOLD, PLATINUM)

This group is composed of cations which are precipitated as sulfides by hydrogen sulfide from solutions which are 0.3 *N* in acid. It includes mercuric mercury, lead, copper, bismuth, cadmium, arsenic, antimony and tin. Silver and mercurous cations are also precipitated by the introduction of hydrogen sulfide into solutions which are 0.3 *N* in acid but it is assumed that they have been removed as chlorides in Group I. Lead is always found in this group for its removal as chloride is incomplete unless the concentration of the hydrochloric acid is carefully adjusted and alcohol is added. A number of rarer elements belong to this group as will be shown in Part V.

MERCURY, Hg

The properties of the element itself, the reactions of mercurous salts, the dry reactions and the detection of mercury in urine have already been discussed under Group I.

Mercuric Salts

Mercuric salts are mostly colorless. The iodide is red or yellow. By heating the red, tetragonal crystals of mercuric iodide, a yellow sublimate of orthorhombic needles is obtained, which gradually changes back to the red tetragonal modification. If the yellow crystals are rubbed the change takes place almost instantly. It is a general property of dimorphous bodies that *the more symmetrical form is almost always the more stable.*

The sulfide is black or red.

Mercuric chloride is soluble in water, 100 ml of water dissolving 6.57 g at 10°, 7.39 g at 20°, 11.34 g at 50°, 24.3 g at 80°, and 53.96 g at 100.°

Mercuric bromide is distinctly less soluble than the chloride (1 g $HgBr_2$ dissolves in 94 ml water at 9°), and mercuric iodide is very much less soluble. The halides of mercury form stable complexes with excess halogen hydride or with alkali chloride, whereby the solubility is increased very materially and the tendency for the mercury halide to volatilize during evaporation is lessened. Small quantities of mercury are always lost when a hydrochloric acid solution is evaporated to dryness and particularly if the residue is heated to dehydrate silica. On the other hand, there is little volatilization of $HgBr_2$ when a solution containing considerable hydrobromic acid is boiled but not evaporated entirely to dryness.

The aqueous solutions of mercuric halide or cyanide are ionized but very slightly into simple mercuric ions.

Mercuric compounds are characterized furthermore by the readiness with which they undergo hydrolysis, forming insoluble basic salts. Thus the sulfate is decomposed when diluted with considerable water (particularly on warming) into a yel-

low insoluble basic salt:

$$3\ HgSO_4 + 2\ H_2O \rightarrow 2\ H_2SO_4 + Hg_3O_2SO_4$$

Hydrogen ions prevent this hydrolysis.

The nitrate also is readily hydrolyzed into more or less insoluble basic salts, according to the dilution:

$$Hg(NO_3)_2 + H_2O \rightleftarrows HNO_3 + Hg(OH)NO_3$$

or

$$2\ Hg(NO_3)_2 + 2\ H_2O \rightleftarrows Hg_2O(OH)NO_3 + 3\ HNO_3$$

All the soluble salts of mercury are poisonous.

Reactions in the Wet Way

A solution of mercuric chloride and one of mercuric nitrate are used for these reactions.

1. **Hydrogen Sulfide** produces in solutions of mercuric salts a precipitate which is at first white, then yellow, brown, and finally black. The white precipitate is formed according to the following equation:

$$3\ HgCl_2 + 2\ H_2S \rightarrow 4\ HCl + Hg_3Cl_2S_2$$

By the further action of hydrogen sulfide, black mercuric sulfide is finally obtained:

$$Hg_3Cl_2S_2 + H_2S \rightarrow 2\ HCl + 3\ HgS$$

Mercuric sulfide is insoluble in dilute boiling acids. Hot concentrated nitric acid transforms it gradually into white $Hg_3S_2(NO_3)_2$,

$$9\ HgS + 8\ HNO_3 \rightarrow 2\ NO\uparrow + 3\ S + 4\ H_2O + 3\ Hg_3S_2(NO_3)_2$$

which by long boiling is changed into the soluble nitrate.

It dissolves readily in aqua regia, forming the chloride with separation of sulfur:

$$3\ HgS + 6\ HCl + 2\ HNO_3 \rightarrow 3\ HgCl_2 + 3\ S + 2\ NO\uparrow + 4\ H_2O$$

Mercuric sulfide is insoluble in caustic soda and potash solutions, and in ammonium sulfide, but it dissolves readily in sodium or potassium sulfide:

$$HgS + S^{--} \rightarrow HgS_2^{--}$$

By dilution with water this complex anion is completely hydrolyzed into mercuric sulfide with the formation of hydrosulfide and hydroxide ions:

$$HgS_2^{--} + H_2O \rightleftarrows OH^- + SH^- + HgS$$

Therefore it is always necessary to dissolve the mercuric sulfide with considerable potassium sulfide, or with little potassium sulfide and considerable caustic potash, in order to prevent this hydrolysis.

The fact that K_2HgS_2 is so readily hydrolyzed explains the formation of cinnabar in nature. In the interior of the earth the thio-compound is formed, which is brought by springs to the surface and there undergoes the above decomposition.

Ammonium chloride precipitates mercuric sulfide from its solution in alkaline sulfide. Unlike the sulfides of silver, lead, bismuth, and cadmium, mercuric sulfide is soluble in potassium thiocarbonate solution, and unlike palladium, it is precipitated from such a solution by means of carbon dioxide gas.

2. **Alkali Hydroxides** precipitate yellow mercuric oxide:

$$HgCl_2 + 2\,OH^- \rightarrow 2\,Cl^- + H_2O + HgO$$

The hydroxides of the noble metals are exceedingly unstable; they lose water, as a rule, even in aqueous solution, forming the anhydrous oxide.

On adding a lesser amount of caustic potash to a solution of mercuric chloride, a reddish brown precipitate of basic chloride is obtained:

$$2\,HgCl_2 + 2\,OH^- \rightarrow 2\,Cl^- + H_2O + Hg_2OCl_2$$

or

$$3\,HgCl_2 + 4\,OH^- \rightarrow 4\,Cl^- + 2\,H_2O + Hg_3O_2Cl_2$$

In the presence of ammonium chloride, the precipitate formed by caustic alkalies is neither yellow nor red, but white as when ammonium hydroxide is added.

Mercuric oxide and the basic salts are readily soluble in acids.

3. **Alkali Bicarbonates** produce no precipitation in a solution of mercuric chloride, but do cause precipitation from mercuric nitrate:

$$4\,Hg(NO_3)_2 + 8\,NaHCO_3 \rightarrow 8\,NaNO_3 + 4\,H_2O + 7\,CO_2\uparrow + Hg_4O_3CO_3$$

4. **Alkali Carbonates** precipitate from both the chloride and the nitrate a reddish brown basic carbonate in the cold:

$$4\,HgCl_2 + 4\,Na_2CO_3 \rightarrow 8\,NaCl + 3\,CO_2\uparrow + Hg_4O_3CO_3$$

which on boiling loses carbon dioxide and is changed into yellow mercuric oxide.

5. **Aluminum, Copper, Zinc, Iron,** and **Formic Acid** precipitate mercury from solutions of its salts:

$$HgCl_2 + 2\,Cu \rightarrow Cu_2Cl_2 + Hg$$

$$HgCl_2 + Fe \rightarrow Fe^{++} + 2\,Cl^- + Hg$$

$$HgCl_2 + HCHO_2 \rightarrow Hg + 2\,HCl + CO_2\uparrow$$

On placing a drop of mercury solution (whether of a mercurous or a mercuric salt) upon a piece of bright copper-foil, a gray spot is formed, which, when dry, becomes as bright as silver by rubbing.

Aluminum placed in a solution containing a mercury salt causes deposition of mercury. The free mercury amalgamates with the aluminum and makes it sensitive to oxidation in moist air. When the aluminum is oxidized to alumina, the mercury unites with more of the aluminum and a trace of mercury causes considerable corrosion of a piece of bright aluminum. The alumina formed can be detected by the alizarin test (see Group III). As little as 0.0001 γ of mercury has been detected by this activation of aluminum.

6. **Neutral Alkali Chromates** precipitate yellow mercuric chromate from both the chloride and nitrate solutions. On long standing or on boiling, the precipitate becomes red, a basic salt probably being formed.

7. **Alkali Dichromates** throw down a yellowish brown precipitate from the nitrate solution, but not from the chloride.

8. **Ammonia** produces in a solution of mercuric chloride a white precipitate of mercuric aminochloride:

$$HgCl_2 + 2\,NH_3 \rightarrow NH_4^+ + Cl^- + Hg(NH_2)Cl$$

This compound, the so-called "infusible precipitate," can be volatilized without melting. It is soluble in acids, and reacts with hot ammonium chloride solution to form the "fusible precipitate":

$$\mathbf{Hg(NH_2)Cl} + NH_4Cl \rightarrow \mathbf{Hg(NH_3)_2Cl_2}$$

If ammonia is allowed to act upon mercuric nitrate a white oxy-amino compound is always formed:

$$2\,Hg(NO_3)_2 + 4\,NH_3 + H_2O \rightarrow 3\,NH_4NO_3 + O\begin{matrix}\diagup \mathbf{Hg} \diagdown \\ \diagdown \mathbf{Hg} \diagup\end{matrix}\mathbf{NH_2 \cdot NO_3}$$

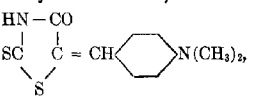
9. **Ammonium Stannic Chloride** and **Sodium Hypophosphite** react rapidly in the presence of mercuric salts.

The reaction

$$2\,Sn^{++++} + H_2PO_2^- + 2\,H_2O \rightarrow 2\,Sn^{++} + PO_4^{---} + 6\,H^+$$

takes place very slowly and incompletely, but if a very little mercuric salt is present, the rate of reaction is increased greatly. This is an *induced reaction*. The presence of Sn^{++} can be shown by cacotheline which gives a violet color. As little as 0.1 γ of mercury can be detected.

10. ***p*-Dimethylaminobenzylidenerhodanine,**



gives a violet or pink precipitate with mercuric solutions. As reagents, prepare a saturated solution of *p*-dimethylaminobenzylidenerhodanine in ethyl alcohol and a saturated solution of sodium acetate in water. Place 1 drop of the solution to be tested on a spot plate and add a drop of each of the two reagents; if 0.33 γ of mercury is present, a pink color will be obtained. Since the reagent mixture itself has a yellow or orange color, when treated with alkali acetate, it is best to make a blank test at the same time. Silver and copper ions cause interference.

11. **Diphenylcarbazide,** $CO(NH \cdot NHC_6H_5)_2$, added to an acid solution of mercuric salt gives a violet or blue precipitate. The composition of the precipitate is doubtful, but it is probably a complex compound of mercury with diphenylcarbazide or with its oxidation product, diphenylcarbazone, $CO\begin{matrix}\diagup NH \cdot NHC_6H_5 \\ \diagdown N = NC_6H_5\end{matrix}$.

The sensitivity of the test depends upon the acidity of the solution and upon whether the mercury is present as halogen salt or not. Increasing acidity lowers the sensitivity, and slightly ionized mercuric chloride reacts much less readily than the nitrate, sulfate, or acetate. In neutral solutions, the reagent gives color reactions with copper, iron, cobalt, and other ions, but in 0.2 *N* nitric acid the test is specific for mercury when chromates and molybdates are absent. In acid of this concentration, 1 γ of mercury as nitrate can be detected as follows:

Place a drop of the solution to be tested on filter paper which has been moistened with a freshly prepared 1 per cent solution of diphenylcarbazide in alcohol.

12. **Diphenylcarbazone,** $CO\begin{matrix}\diagup NH \cdot NHC_6H_5 \\ \diagdown N = NC_6H_5\end{matrix}$, gives an orange compound soluble in carbon tetrachloride. As little as 0.25 γ of mercury as $HgCl_2$ will give the test. Many other cations react with the reagent to give colored compounds, but if the test

is made in an acid solution, the only elements that interfere seriously are Sn, Sb, Bi, Cu, Au, and the platinum metals. The trivial name *dithizone* has been proposed for diphenylcarbazone.

Mix 1 drop of the solution to be tested with 2 drops of the green solution obtained by dissolving 6–20 mg of dithizone in 1 l of carbon tetrachloride. After the evaporation of the liquid, add a little carbon tetrachloride; an orange solution will be obtained if mercury is present.

The interference of ferrous and stannous ions can be prevented by oxidation; the reactions of the reagent with antimony and bismuth can be prevented by adding tartaric acid together with a little nitric acid in the case of bismuth. Gold ions can be precipitated with sulfurous acid and platinum metals removed by treatment with powdered copper or silver. If copper is present, the mercury solution should be neutralized and then made distinctly acid by adding 95 per cent formic acid. Then on adding dithizone solution a pink color will be obtained which turns to orange yellow if mercury is present.

13. **Ferrous Sulfate** reduces mercuric nitrate on boiling to metallic mercury:

$$Hg(NO_3)_2 + 2\ Fe^{++} \rightarrow 2\ Fe^{+++} + 2\ NO_3^- + Hg$$

Mercuric chloride and cyanide are not reduced by ferrous sulfate.

14. **Potassium Cyanide** produces in a solution of mercuric chloride no precipitation, because the cyanide, as well as the chloride, forms readily soluble complex compounds with alkali chlorides. The following are known: $K[HgCl_3]$, $K_2[HgCl_4]$ $K[Hg(CN)_2Cl]$, $K_2[Hg(CN)_2Cl_2]$, and $K_2[Hg(CN)_4]$.

In a concentrated solution of mercuric nitrate, potassium cyanide produces a precipitate of mercuric cyanide, soluble in considerable water and in potassium cyanide:

$$Hg(NO_3)_2 + 2\ CN^- \rightarrow 2\ NO_3^- + Hg(CN)_2$$

Mercuric cyanide is the only cyanide of the heavy metals that is soluble in water. Such a solution dissolves mercuric oxide perceptibly, forming the complex compound $(HgCN)_2O$. A solution of mercuric cyanide gives no precipitate with carbonates or caustic alkalies, because mercuric oxide is soluble in mercuric cyanide. Mercuric cyanide is not decomposed by dilute sulfuric acid, although it is by the halogen acids — most difficultly by hydrochloric acid, and most readily by hydriodic acid; hydrogen sulfide decomposes it with precipitation of mercuric sulfide:

$$Hg(CN)_2 + H_2S \rightarrow 2\ HCN + HgS$$

15. **Potassium Iodide** produces a red precipitate of mercuric iodide,

$$HgCl_2 + 2\ I^- \rightarrow 2\ Cl^- + HgI_2$$

soluble in excess iodide ions, forming a colorless complex anion:

$$HgI_2 + 2\ I^- \rightarrow [HgI_4]^{--}$$

This complex anion is scarcely dissociated at all into simple mercuric cations, for the solution gives no precipitate with caustic soda or potash. The alkaline solution is the so-called Nessler's reagent, and serves for the detection of very slight traces of ammonia. There is formed in this reaction the brown-colored compound, $O\langle{}^{Hg}_{Hg}\rangle NH_2 \cdot I$, which is soluble in an excess of the Nessler's reagent, with an intense yellow color (cf. Group V). Small quantities of mercury can also be detected by means of this reaction, in which case caustic alkali and ammonia are added to the solution which has been tested with potassium iodide.

16. **Potassium Thiocyanate** added to mercuric *nitrate* solution gives a white precipitate of $Hg(CNS)_2$. Mercury can be determined quantitatively by measuring the volume of thiocyanate solution which can be added before a permanent red color is produced with a little ferric salt which has been added as indicator. Silver is determined similarly.

17. **Sodium Thiosulfate** added to a boiling acid solution of mercuric salt gradually precipitates HgS and S:

$$Hg^{++} + 3\ S_2O_3^{--} + 2\ H^+ \rightarrow \mathbf{HgS} + 2\ S + SO_4^{--} + H_2O + 2\ SO_2$$

18. **Stannous Chloride** reduces mercuric salts, first to insoluble mercurous chloride (calomel):

$$2\ HgCl_2 + Sn^{++} \rightarrow Sn^{++++} + \mathbf{Hg_2Cl_2} + 2\ Cl^-$$

and by further action to free mercury:

$$\mathbf{Hg_2Cl_2} + Sn^{++} \rightarrow Sn^{++++} + 2\ \mathbf{Hg} + 2\ Cl^-$$

Metallic mercury separates out in the form of a gray powder. By decanting the solution, and boiling the residue with dilute hydrochloric acid, the mercury appears in tiny globules.

LEAD, Pb

The properties of the element and of its compounds were given under Group I, page 110.

BISMUTH, Bi. At. Wt. 209.0, At. No. 83

Density 9.8. M. P. 271°. B. P. 1490°

Occurrence. — Bismuth usually occurs native with nickel and cobalt ores. The following ores are of no great importance: Bismite, Bi_2O_3; bismuthinite, Bi_2S_3; emplectite, $Bi_2S_4Cu_2$; bismutite, $3\ (BiOH)(CO_3) \cdot 5\ Bi(OH)_3$.

Properties. — Bismuth is a brittle, reddish white metal which crystallizes in the hexagonal system. It was discovered by Valentine in 1450, and its name is derived from the German *Wismut*, which in turn was derived from *Wiesemutung*. When heated to 1200° the metal begins to volatilize as its vapor pressure is then 102 mm. Bismuth is diatomic in the solid state (metals are usually monatomic), but the vapor is monatomic. About 270 tons of the metal are produced annually. It is a constituent of some low-melting alloys, and its oxide and salts are used in many pharmaceutical preparations. *Nitric acid is the proper solvent for bismuth:*

$$Bi + 4\ HNO_3 \rightarrow Bi(NO_3)_3 + 2\ H_2O + NO\uparrow$$

The metal is insoluble in hydrochloric acid but is dissolved by hot, concentrated sulfuric acid;

$$2\ Bi + 6\ H_2SO_4 \rightarrow Bi_2(SO_4)_3 + 3\ SO_2\uparrow + 6\ H_2O$$

Bismuth will dissolve in hydrochloric or acetic acid if some concentrated hydrogen peroxide (perhydrol) is added. Aqua regia dissolves it, forming bismuth trichloride.

Bismuth forms three oxides: bismuth trioxide, Bi_2O_3; bismuth tetroxide, Bi_2O_4; and bismuth peroxide, Bi_2O_5.

Bismuth trioxide is a basic anhydride,* from which most bismuth salts are derived.

Bismuth pentoxide, a brownish substance, acts as an acid anhydride, forming an acid, HBiO, corresponding to metaphosphoric acid. Salts of this acid have never been prepared in a pure state. On igniting, Bi_2O_5 loses oxygen, forming yellow Bi_2O_3. It dissolves in hydrochloric acid with evolution of chlorine, forming a salt of trivalent bismuth:

$$Bi_2O_5 + 10\ HCl \rightarrow 5\ H_2O + 2\ BiCl_3 + 2\ Cl_2 \uparrow$$

Bismuth tetroxide is a brown powder which is sometimes used as an efficient oxidizing agent. Commercial sodium bismuthate is probably a mixture of $NaBiO_3$ and Bi_2O_4.

Bismuth salts are mostly colorless, and are all insoluble in considerable water, on account of being hydrolyzed into an insoluble basic salt; thus the chloride is quantitatively decomposed into basic bismuth chloride, often called *bismuthyl* chloride,

$$BiCl_3 + H_2O \rightleftarrows 2\ HCl + BiOCl$$

insoluble in tartaric acid (difference from antimony).

Bismuthyl chloride is readily soluble in hydrochloric acid, the above equation taking place from right to left. The reaction, therefore, is reversible, and the relative amounts of water and hydrochloric acid present determine in which direction the reaction will go. On adding water to a slightly acid solution of $BiCl_3$, a white precipitate of the basic chloride appears immediately. On carefully adding hydrochloric acid, the precipitate again dissolves, but may be reprecipitated by the addition of more water. All the other compounds of bismuth act as the chloride. The nitrate yields, at first, an amorphous precipitate of $BiONO_3$,

$$Bi(NO_3)_3 + H_2O \rightleftarrows 2\ HNO_3 + BiO(NO_3)$$

which becomes more basic and crystalline on further addition of water:

$$2\ BiO(NO_3) + H_2O \rightleftarrows Bi_2O_2(OH)(NO_3) + HNO_3$$

This last compound is the *bismuth subnitrate* which is so much used in medicine.

Reactions in the Wet Way

1. **Hydrogen Sulfide** precipitates brown bismuth sulfide:

$$2\ Bi^{+++} + 3\ H_2S \rightarrow Bi_2S_3 + 6\ H^+$$

insoluble in cold dilute mineral acids and alkaline sulfides, soluble in hot dilute nitric acid and in boiling concentrated hydrochloric acid.

$$Bi_2S_3 + 8\ H^+ + 2\ NO_3^- \rightarrow 2\ Bi^{+++} + 2\ NO \uparrow + 4\ H_2O + 3\ S$$

2. **Alkali Carbonates** precipitate, according to the temperature and concentration, a number of basic carbonates, one of which is formed according to the following equation:

$$2\ Bi^{+++} + 3\ CO_3^{--} + H_2O \rightleftarrows 2\ Bi(OH)(CO_3) + CO_2 \uparrow$$

* Bismuth trioxide acts as a weak acid under some circumstances (cf. footnote, p. 125).

3. **Alkali Hydroxides** precipitate, in the cold, white bismuth hydroxide:

$$Bi^{+++} + 3\,OH^- \rightarrow \mathbf{Bi(OH)_3}$$

which, on boiling, becomes pale yellow:

$$\mathbf{Bi(OH)_3} \rightarrow H_2O + \mathbf{BiO(OH)}$$

Both these hydroxides are insoluble in an excess of the precipitant,* but are readily soluble in acids.

On adding to the alkaline solution, in which the hydroxide is suspended, chlorine, bromine, hypochlorites, or hydrogen peroxide, the white or yellowish precipitate becomes brown, owing to the formation of bismuthic acid:

$$\mathbf{BiO(OH)} + 2\,OH^- + Cl_2 \rightarrow H_2O + 2\,Cl^- + \mathbf{HBiO_3}$$

4. **Alkali Stannites** (alkaline solutions of stannous chloride) cause a black precipitation of metallic bismuth.† This very sensitive reaction is performed as follows: To a few drops of stannous chloride, add caustic alkali until the white precipitate at first produced dissolves. Add this sodium stannite solution to the cold bismuth solution; on shaking, a black precipitate immediately appears. The following reactions take place in this test:

$$Sn^{++} + 2\,OH^- \rightarrow \mathbf{Sn(OH)_2}$$

$$\mathbf{Sn(OH)_2} + 2\,OH^- \rightarrow 2\,H_2O + SnO_2^{--}$$

$$3\,SnO_2^{--} + 2\,B^{+++} + 6\,OH^- \rightarrow 3\,H_2O + 3\,SnO_3^{--} + \mathbf{2\,Bi}$$

In making this test, a too concentrated caustic alkali solution should be avoided and the solution must be kept cold, otherwise the stannite itself may give a black precipitate of metallic tin (cf. pp. 168, 228):

$$2\,SnO_2^{--} + H_2O \rightarrow SnO_3^{--} + 2\,OH^- + \mathbf{Sn}$$

If too little caustic potash is used, black stannous oxide will be thrown down in the cold, after long standing; quickly on boiling:

$$SnO_2^{--} + H_2O \rightarrow 2\,OH^- + SnO$$

5. **Alkali Stannite and Lead Salt.** If a drop of 1 per cent lead acetate solution is mixed on a spot plate with a drop of alkali stannite solution, there will be no darkening due to deposition of lead until after three to ten minutes. The reaction:

$$PbO_2^{--} + SnO_2^{--} + H_2O \rightarrow \mathbf{Pb} + SnO_3^{--} + 2\,OH^-$$

takes place very slowly, but if a trace of bismuth is present (less than the quantity

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* In very concentrated KOH, $Bi(OH)_3$ dissolves on warming. On cooling, part of the $Bi(OH)_3$ is precipitated, and on dilution all of it. In this case the hydroxide acts as a weak acid, like antimony trioxide.

† Vanino and Treubert, *Ber.*, **1898**, 1113. The precipitate often contains BiO.

required to show visible reduction to bismuth, in the alkali stannite test) the reduction of the lead is catalyzed and takes place much more rapidly.

Place a drop of the hydrochloric acid solution to be tested for bismuth, on a spot plate, add 1 drop of saturated lead chloride solution and 2 drops of alkali stannite reagent, and mix by stirring. A distinct brownish color will be obtained with 0.01 γ of bismuth within three minutes. If much bismuth is present, a precipitate of metallic lead will be obtained immediately. To prepare the alkali stannite reagent, dissolve 5 g of stannous chloride crystals in 5 ml of concentrated hydrochloric acid and dilute with water to 100 ml. When ready to make the test, mix a little of the stannous chloride with an equal volume of 25 per cent sodium hydroxide solution.

Copper interferes because brown cuprous oxide is formed slowly by the action of alkali stannite. To prevent interference, add after the drop of saturated lead chloride, 1 drop of 2 *N* sodium hydroxide and 1 drop of 5 per cent potassium cyanide solution and then add the stannite. In this way 1 γ of bismuth can be detected in the presence of 1 mg of copper.

6. **Ammonia** precipitates a white basic salt (not the hydroxide), the composition of which varies with the concentration and with the temperature.

7. **Ammonium Thioacetate** causes the partial precipitation of bismuth sulfide in the cold and complete precipitation on boiling:

$$3\ CH_3COS^- + 2\ Bi^{+++} + 3\ H_2O \rightarrow 3\ CH_3COOH + Bi_2S_3 + 3\ H^+$$

Sodium thiosulfate added to a solution of a bismuth salt containing not too much acid, gives at first a yellow coloration and finally a black precipitate of sulfide:

$$3\ H_2O + 2\ Bi^{+++} + 3\ S_2O_3^{--} \rightarrow Bi_2S_3 + 6\ H^+ + 3\ SO_4^{--}$$

8. **Cinchonine** and **Potassium Iodide** added to a slightly acid solution containing bismuth ions causes precipitation or an orange-red coloration due to the formation of bismuth-cinchonine iodide. The test has been obtained with as little as 0.14 γ of bismuth.

Cinchonine is an organic base of complicated composition. It, as well as numerous other organic bases, forms insoluble double iodides with bismuth of the general formula $BiI_3 \cdot B \cdot HI$ in which B represents the base. These organic bases can be regarded as molecules of NH_3 with one or more of the hydrogen atoms replaced by organic groups. Just as we can write ammonium iodide $NH_3 \cdot HI$, so it is quite common merely to add the formula of the acid to that of the base in forming salts of organic bases. What we call an organic base is usually a compound like NH_3 rather than one like NH_4OH (which can also be written $NH_3 \cdot H_2O$).

To prepare the reagent for the above test, dissolve 1 g of cinchonine in 100 ml of hot water and a little nitric acid; cool and add 2 g of potassium iodide.

The presence of copper, lead, and mercury interferes with the test as these elements react with potassium iodide. If, however, the test is made on filter paper, the test spot, as a result of capillarity, usually shows distinct zones; a white central zone contains the mercury, around it is an orange ring due to bismuth, next comes a yellow ring due to lead iodide, and on the outside is a brown ring caused by free iodine liberated by the reaction with Cu^{++}.

Procedure. — Moisten a piece of filter paper with the cinchonine reagent, and upon the moistened spot put a drop of the slightly acid solution to be tested. An orange-red spot indicates the presence of bismuth.

9. **Potassium Cyanide** precipitates the white hydroxide (not the cyanide). The cyanide is probably formed first, but it is hydrolyzed:

$$Bi^{+++} + 3\,CN^- \rightarrow \mathbf{Bi(CN)_3}$$

$$\mathbf{Bi(CN)_3} + 3\,HOH \rightarrow 3\,HCN + \mathbf{Bi(OH)_3}$$

10. **Potassium Dichromate** added in excess precipitates yellow bismuthyl dichromate:

$$Cr_2O_7^{--} + 2\,Bi^{+++} + 2\,H_2O \rightarrow 4\,H^+ + \mathbf{(BiO)_2Cr_2O_7}$$

soluble in mineral acids, insoluble in caustic alkalies (difference from lead whose sulfate is less readily dissolved by acids but dissolves readily in solutions of caustic alkali).

11. **Potassium Iodide** precipitates black bismuth iodide,

$$Bi^{+++} + 3\,I^- \rightarrow \mathbf{BiI_3}$$

soluble in excess of the reagent, forming a yellow or orange solution:

$$\mathbf{BiI_3} + I^- \rightarrow [BiI_4]^-$$

By diluting this last solution with not too much water, the black iodide is reprecipitated, which, on the addition of more water, is changed into orange-colored basic iodide:

$$\mathbf{BiI} + H_2O \rightarrow 2\,HI + \mathbf{BiOI}$$

12. **Sodium Phosphate** precipitates the white, granular phosphate, insoluble in dilute nitric acid, difficultly soluble in hydrochloric acid:

$$2\,HPO_4^{--} + Bi^{+++} \rightarrow H_2PO_4^- + \mathbf{BiPO_4}$$

13. **Sulfuric Acid** does not cause precipitation when added to acid solutions of bismuth salts. When the solution is evaporated until fumes of sulfuric acid are evolved, the resulting bismuth acid sulfate will dissolve in water giving a clear solution in most cases. After standing a long time, or sooner if considerable bismuth is present, a white precipitate of bismuthyl pyrosulfate, $(BiO)_2S_2O_7 \cdot 3\,H_2O$, forms, and this is sometimes mistaken for lead sulfate in the analytical procedure.

14. **Water** causes hydrolysis of all soluble bismuth salts and insoluble basic salts are precipitated. This is particularly true of the chloride:

$$Bi^{+++} + Cl^- + H_2O \rightarrow \mathbf{BiOCl} + 2\,H^+$$

The precipitate dissolves readily in dilute, mineral acid, but, unlike antimonyl chloride, SbOCl, it is not dissolved by tartaric acid. The precipitation of bismuthyl chloride is a characteristic reaction of bis-

muth and may take place, to some extent at least, when a chloride or even hydrochloric acid is added to a solution of bismuth nitrate.

15. **Zinc** precipitates metallic bismuth:

$$2\,Bi^{+++} + 3\,Zn \rightarrow 3\,Zn^{++} + 2\,Bi$$

Reactions in the Dry Way

Bismuth salts color the non-luminous flame a pale greenish white. Heated with soda on charcoal before the blowpipe, a brittle button of the metal is obtained, surrounded by a yellow incrustation of bismuth oxide.

The flame test for bismuth can be made to detect as little as 0.004 γ of bismuth. Ignite, gently, in a hydrogen flame which is not more than 0.5 cm long, a paste of calcium carbonate and water in a loop of platinum wire. This dries the paste and causes some calcium oxide to be formed. By means of another platinum wire loop, moisten the ignited product with a drop of the solution to be tested and heat again but not too strongly. Cool for a short time and then bring the mass near the edge of the hydrogen flame; if bismuth is present a blue luminescence will be obtained the moment the mass touches the flame. When the lime begins to glow, the bismuth test will be obscured.

On heating a compound of bismuth in the upper reducing flame (p. 78) of the Bunsen burner, the bismuth is reduced to metal, which is volatilized and burnt to oxide in the upper oxidizing flame. On holding a porcelain evaporating dish (glazed on the outside and filled with water) just above the oxidizing flame, a barely visible deposit is obtained, which, on being treated with hydriodic acid, is changed to scarlet iodobismuthic acid:

$$Bi_2O_3 + 8\,HI \rightarrow 3\,H_2O + 2\,H[BiI_4]$$

The hydriodic acid is most easily obtained by moistening a piece of asbestos, held in the loop of a platinum wire, in a solution of alcoholic iodine solution and then setting fire to the moist asbestos. By holding the burning asbestos under the dish, enough hydriodic acid is obtained to change the bismuth oxide into the red compound.

By breathing on this deposit, the color disappears, but reappears as soon as the moisture has evaporated. On exposure to fumes of ammonia (by blowing the vapors away from the stopper of an ammonia bottle) the deposit is colored a beautiful orange, owing to the formation of the ammonium salt of the iodobismuthic acid:

$$H[BiI_4] + NH_3 \rightarrow NH_4[BiI_4]$$

which also becomes invisible on being breathed upon.

By moistening this coating with an alkaline solution of stannous chloride, black metallic bismuth is deposited.

COPPER, Cu. At. Wt. 63.57, At. No. 29

Density 8.93. M. P. 1083° C. B. P. about 2310°

Occurrence. — Copper occurs as native copper, Cu; cuprite, Cu_2O; chalcocite, Cu_2S; chalcopyrite, $CuFeS_2$; malachite, $Cu_2(OH)_2CO_3$; azurite, $Cu_3(OH)_2(CO_3)_2$; and atacamite, $Cu_2O(OH)Cl{\cdot}H_2O$.

Properties. — Copper is a light red ductile metal; its name is derived from the Latin *cuprum*, which is related to the fact that copper was obtained in ancient times from the island of Cyprus. The metal was known in prehistoric times (more than 6,000 years ago). In tenacity, it is next to iron, although a copper wire will support only half of the weight borne by an iron wire of the same size. As a conductor of heat it is surpassed by gold and silver, and it is next to silver as a conductor of electricity. The effect of even a slight impurity, especially arsenic, is very marked upon the conductivity of the metal. Dry air does not oxidize copper, but in moist air containing carbon dioxide it becomes covered with a layer of basic carbonate, called *verdigris*, which protects the metal from corrosion. Water alone has no appreciable action, but hot water containing dissolved oxygen causes corrosion. Important alloys of copper are brass, bronze, and German silver. The annual production of copper is over 1,500,000 tons, of which about half is mined in the United States. Its price has fluctuated in recent years from 6 to 30 cents per pound.

The proper solvent for copper is nitric acid:

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu^{++} + 6\ NO_3^- + 4\ H_2O + 2\ NO\uparrow$$

Bright copper is not dissolved by hydrochloric acid alone, but in the presence of a weak oxidizing agent, *e.g.*, ferric chloride, the solution of the metal is easily effected. Hot hydrobromic acid dissolves it with evolution of hydrogen, forming bromocuprous acid:

$$2\ Cu + 6\ HBr \rightleftarrows H_4[Cu_2Br_6] + H_2\uparrow$$

At the beginning of this reaction the solution usually turns dark violet on account of the formation of the cupric salt of bromocuprous acid, owing to the copper being somewhat oxidized on the surface. In this case, however, the solution soon becomes colorless, owing to the reduction of the cupric salt by metallic copper. On adding water to the clear solution cuprous bromide is precipitated:

$$[Cu_2Br_6]^{=} \rightarrow Cu_2Br_2 + 4\ Br^-$$

Copper is not attacked by dilute sulfuric acid, but it dissolves in hot concentrated sulfuric acid, forming cupric sulfate with evolution of sulfur dioxide:

$$Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + 2\ H_2O + SO_2\uparrow$$

The behavior of copper toward acids can be understood by reference to the electromotive series (p. 43). Since copper is below hydrogen in the series it can be oxidized by hydrogen ions only when the concentration of cupric ions is kept very low (cf. p. 40). Hydrobromic acid dissolves copper because a slightly ionized complex is formed. Sulfuric acid dissolves copper by virtue of the oxidizing power of the hexavalent sulfur.

According to statements in the literature, copper forms four oxides, Cu_2O, CuO, Cu_2O_3, and CuO_2, but the only oxides which actually have been isolated are red cuprous oxide, Cu_2O, and black cupric oxide, CuO. Cuprous oxide can be obtained by heating an alkaline tartrate solution of copper (Fehling's solution) with an arsenite or with a reducing sugar, such as *d*-glucose. This reaction is used a great deal in sugar analysis. Cuprous oxide, Cu_2O, can also be made by heating cupric oxide with copper or by reducing a cupric solution with hydroxylamine, NH_2OH, in the presence of a base. Black cupric oxide, CuO, can be made by heating copper or its hydroxide, carbonate, sulfate, nitrate, etc., in the air. Copper peroxide, CuO_2, and copper sesquioxide, Cu_2O_3, are of no importance if they exist.

Both cuprous and cupric oxides are basic anhydrides, forming cuprous and cupric

salts. Salts of the cuprous series contain the bivalent cuprous group, Cu_2^{++}; those of the cupric series contain the simple, bivalent copper ion Cu^{++}.

Copper is also known in the trivalent condition.* If a nitric acid solution of tellurous acid is evaporated to dryness with a little copper nitrate and the residue is treated with KOH solution (1 : 5) it dissolves. If to the clear solution 4 to 6 g of $(NH_4)_2SO_4$ are added, little by little, while the solution is at the temperature of the water bath, it becomes pink and the tellurium is present for the most part as telluric acid but to some extent as the potassium salt of telluro-cupric acid:

$$K[O \cdot Cu\begin{matrix}O\\O\end{matrix}TeO_2]$$

A. Cuprous Compounds

The cuprous compounds are extremely unstable, being oxidized quickly to cupric compounds. The best-known cuprous salts are those with the halogens, the thiocyanate, the complex cyanides, the very unstable sulfate, and the sulfite. Cuprous salts are colorless, insoluble in water, but readily soluble in concentrated halogen acids, forming colorless solutions. Such solutions contain the unstable cuprous halogen acids, probably of the formula $H_4[Cu_2X_6]$, in which "X" is either chlorine, bromine, or iodine. Salts are known which are derived from these acids, *e.g.*, $K_4[Cu_2Cl_6]$.

The cuprous halogen acids are darkened by contact with air. The chloride becomes brownish black; the bromide, dark violet; probably owing to the formation of cupric salts of the cuprous halogen acids.

The behavior of the cuprous halogen acids toward carbon monoxide is very important; the carbon monoxide is readily absorbed, forming an unstable compound:

$$H_2Cu_2Cl_4 + 2\,CO + 2\,H_2O \rightleftarrows Cu_2Cl_2 \cdot 2\,CO \cdot 2\,H_2O + 2\,HCl$$

By boiling the solution the compound is decomposed into cuprous chloride and carbon monoxide. Cuprous chloride is used in gas analysis for the absorption of this gas.

Reactions in the Wet Way

A solution of cuprous chloride in hydrochloric acid should be used, which may be prepared as follows: Dissolve 2 g of cupric oxide in 25 ml of 6-normal hydrochloric acid, pour the solution into a flask, and add 1.6 g of copper filings. Place several copper spirals in the flask, one end reaching up to its neck, stopper the flask, invert it, and let it stand several days. The originally dark solution will gradually become colorless and is then ready to be used for the following reactions:

1. **Hydrogen Sulfide** precipitates black cuprous sulfide:

$$Cu_2^{++} + H_2S \rightarrow 2\,H^+ + Cu_2S$$

soluble in warm dilute nitric acid, forming blue cupric nitrate, with separation of sulfur:

$$3\,Cu_2S + 16\,HNO_3 \rightarrow 8\,H_2O + 3\,S + 6\,Cu^{++} + 12\,NO_3^- + 4\,NO\uparrow$$

2. **Potassium Cyanide** precipitates white cuprous cyanide:

$$Cu_2^{++} + 2\,(CN)^- \rightarrow Cu_2(CN)_2$$

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* Cf. Moser, *Z. anorg. Chem.*, **54**, 119 (1907), and Brauner and Kuzma, *Ber.*, **1907**, 3362.

soluble in excess, forming colorless complex cuprocyanide anions:

$$Cu_2(CN)_2 + 6\ (CN)^- \rightarrow [Cu_2(CN)_8]^{====}$$

This solution contains no appreciable quantity of cuprous ions, and gives no precipitation with potassium hydroxide or hydrogen sulfide. It is estimated that in a normal potassium cyanide solution the ratio of the concentration of the complex anions to that of simple cuprous ions is about $10^{28} : 1$. This fact is utilized in the separation of copper from cadmium.

In the absence of an excess of CN^- ions, however, an appreciable ionization takes place: $[Cu_2(CN)_8]^{====} \rightarrow Cu_2^{++} + 8\ CN^-$, and this ionization increases as the solution is diluted. From the diluted solutions the compounds $K_2[Cu_2(CN)_4]$, $K[Cu_2(CN)_3]$, and finally $Cu_2(CN)_2$ are obtained, which are of less complex nature.

All these compounds, even in the solid state, are decomposed by hydrogen sulfide with precipitation of black cuprous sulfide. Consequently, *in order to prevent the precipitation of copper by hydrogen sulfide, considerable potassium cyanide must be added, i. e., more than enough to form the salt* $K_3[Cu_2(CN)_8]$.

3. **Potassium Hydroxide** produces in the cold a yellow precipitate of cuprous hydroxide:

$$Cu_2^{++} + 2\ OH^- \rightarrow Cu_2(OH)_2$$

which loses water at the boiling temperature, changing to red cuprous oxide:

$$Cu_2(OH)_2 \rightarrow H_2O + Cu_2O$$

B. Cupric Compounds

Cupric salts are either blue or green in aqueous solution; in the anhydrous state they are white or yellow.

The chloride, nitrate, sulfate, and acetate are soluble in water; most of the remaining salts are insoluble in water, but readily soluble in acids.

Reactions in the Wet Way

A solution of copper sulfate should be used.

1. **Hydrogen Sulfide** precipitates from neutral or acid solutions, black cupric sulfide (possibly mixed with cuprous sulfide, Cu_2S), which has a tendency to form a colloidal solution (p. 64) and run through the filter:

$$Cu^{++} + H_2S \rightarrow 2\ H^+ + CuS$$

To prevent the formation of a colloidal solution, the solution must contain some electrolyte; the hydrochloric acid present when the precipitation is made is usually sufficient. Another difficulty frequently encountered is due to the readiness with which a part of the cupric sulfide precipitate is oxidized to sulfate by contact with the air. Thus if a filter containing copper sulfide is allowed to stand in the air, a little cupric sulfate is formed which is soluble in water. Many cases where the cupric sulfide apparently runs through the filter are explained in this way. In filtering a copper sulfide precipitate the rule should be never to let the filter drain completely until the filtration and washing is over, and the washing should be with acidulated hydrogen sulfide water, which serves to prevent any oxidation.

Copper sulfide is soluble in hot dilute nitric acid:

$$3\ CuS + 8\ H^+ + 2\ NO_3^- \rightarrow 3\ Cu^{++} + 2\ NO\uparrow + 4\ H_2O + 3\ S$$

The sulfide is insoluble in boiling dilute sulfuric acid (difference from cadmium); it is soluble in potassium cyanide, forming potassium cuprocyanide:

$$2\ CuS + 9\ CN^- \rightarrow Cu_2(CN)_3^{---} + CNS^- + S^{--}$$

From a solution of the latter salt the copper cannot be precipitated by hydrogen sulfide.

Copper sulfide is appreciably soluble in ammonium sulfide, but is insoluble in potassium or sodium sulfide* (difference from mercury).

2. **Acetylene** gas introduced into an ammoniacal alkali tartrate solution, in which the copper has been reduced to the cuprous condition by hydroxylamine, gives a reddish brown, flocculent precipitate of cuprous acetylide, $C_2Cu_2 \cdot H_2O$. By this means copper ions can be separated from many other cations.

3. **Alkali Hydroxide** produces in the cold a blue precipitate of cupric hydroxide,

$$Cu^{++} + 2\ OH^- \rightarrow Cu(OH)_2$$

which on boiling becomes changed into brownish black cupric oxide.

$Cu(OH)_2$ is slightly amphoteric in nature and dissolves in very concentrated KOH or NaOH, particularly on warming, with a blue color. (Cf. p. 239.)

In the presence of tartaric acid, citric acid, and many other organic hydroxy-compounds, cupric hydroxide is not precipitated by the addition of caustic alkali, but the solution is colored an intense blue. If this alkaline solution is treated with *d*-glucose, aldehydes, arsenious acid, or various other substances having a reducing power, yellow cuprous hydroxide is precipitated from a warm solution and is changed to red cuprous oxide on boiling. An alkaline solution of cupric salt containing tartrate is commonly used under the name of Fehling's solution. It may be prepared by mixing together equal volumes of a solution containing 34.64 g of crystallized copper sulfate in 500 ml with a solution containing 173 g Rochelle salt and 52 g NaOH in 500 ml. It is best to keep the two solutions apart until the reagent is to be used. Fehling's solution is a reagent for many sugars, aldehydes, hydroxylamine, etc.

4. **Alkali Carbonates** give a greenish blue precipitate of basic carbonate; on standing with an excess of the reagent the precipitation is nearly complete and a crystalline salt, $3\ CuCO_3 \cdot 3\ Cu(OH)_2 \cdot H_2O$, is formed. This precipitate dissolves in ammonia with a blue color and in potassium cyanide solution to form a colorless solution.

Ammonium salts and certain organic substances form complex anions with copper and prevent this reaction.

5. **Alkali Xanthates** produce in solutions of cupric salts, at first, a brownish black precipitate of cupric xanthate, which splits off dixanthogen, forming finally

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* In solutions of alkali polysulfides, particularly out of contact with the air, cupric sulfide dissolves appreciably with the formation of compounds of the type $NH_4[CuS_4]$ and $K[CuS_4]$. Cf. Hofmann and Höchtlen, *Ber.*, **36**, 3090 (1903), and Biltz and Herms, *ibid.*, **40**, 974 (1907).

yellow cuprous xanthate:

$$2\,NaS\cdot\overset{\overset{S}{\|}}{C}\cdot OC_2H_5 + Cu^{++} \rightarrow 2\,Na^+ + Cu(S\cdot\overset{\overset{S}{\|}}{C}\cdot OC_2H_5)_2$$

Sodium xanthate

$$2\,Cu(S\cdot\overset{\overset{S}{\|}}{C}\cdot OC_2H_5)_2 \rightarrow \underset{\text{Cuprous xanthate}}{Cu_2(SCOC_2H_5)_2} + \underset{\text{Dixanthogen}}{(SCOC_2H_5)_2}$$

The reagent, sodium xanthate, is readily obtained by mixing carbon disulfide with sodium ethylate:

$$CS_2 + NaOC_2H_5 \rightarrow NaS\cdot\overset{\overset{S}{\|}}{C}\cdot OC_2H_5$$

The alkali xanthates are not used as reagents in testing for copper, but cupric salts are used in testing for xanthates. The reaction is used for the detection of carbon disulfide in gas mixtures; the gases are allowed to act upon sodium alcoholate, whereby sodium xanthate is formed if carbon disulfide is present, and the solution after neutralizing with acetic acid is tested for xanthate by means of a solution of cupric salt.

6. **Ammonia.** — On adding ammonia cautiously to the solution of a cupric salt, a green, powdery precipitate of a basic salt is obtained, which is extremely soluble in an excess of the reagent, forming an azure-blue solution:

$$2\,CuSO_4 + 2\,NH_4OH \rightarrow (NH_4)_2SO_4 + Cu_2(OH)_2SO_4$$

$$Cu_2(OH)_2SO_4 + (NH_4)_2SO_4 + 6\,NH_3 \rightarrow 2\,([Cu(NH_3)_4]SO_4\cdot H_2O)$$

On adding alcohol to the concentrated blue solution, the above compound is precipitated as blue-violet tetramminecupric sulfate, which gradually loses ammonia on being heated, leaving behind the cupric salt. On conducting ammonia gas over an anhydrous copper salt, the ammonia is eagerly absorbed, with the formation of a complex cupric ammonia salt: $CuCl_2 + 6\,NH_3 \rightarrow [Cu(NH_3)_6]Cl_2$.

These compounds (which contain as a maximum 6 NH_3 to one atom of copper) are perfectly analogous to the corresponding compounds of nickel, cobalt, and zinc. By the precipitation of the ammoniacal solution with alcohol, the compound with 4 NH_3 to one atom of copper is always obtained.

The ionization of the complex cation:

$$[Cu(NH_3)_4]^{++} \rightarrow Cu^{++} + 4\,NH_3\uparrow$$

is slight in the presence of excess ammonia, but much more than that of the cuprocyanide ion (p. 136).

Ammonium salts tend to prevent the precipitation of the basic cupric salt because of the common-ion effect upon the ionization of ammonium hydroxide, so that in adding ammonia to an acid solution of cupric salt often no precipitate is obtained. The blue color of the complex is perceptible even at considerable dilution and is often used to ascertain the quantity of copper present; the copper content is determined colorimetrically or by measuring the volume of standard potassium cyanide solution required to decolorize the solution. Nickelous solutions give a less in-

tense blue color with ammonia, and in case of doubt whether any copper is present in solution, the potassium ferrocyanide test is decisive.

Alkali hydroxide added to the blue, ammoniacal copper solution gives a blue precipitate of cupric hydroxide after some time. On boiling, all the copper can be precipitated as brownish black cupric oxide, CuO. A very dilute copper solution gives no noticeable blue color with ammonia; shaking with a few drops of phenol causes the blue color to appear on standing.

7. **Ammonium Mercurithiocyanate,** $(NH_4)_2Hg(CNS)_4$, added to a solution containing both zinc and cupric ions, gives a deep violet crystalline precipitate of a complex thiocyanate of zinc, copper, and mercury. The test is reliable in the absence of ferric ions, nickel, and cobalt.

To prepare the reagent, dissolve 8 g of $HgCl_2$ and 9 g of NH_4CNS in 100 ml of water.

Place 1 drop of the acid solution to be tested on a spot plate, add 1 drop of 1 per cent zinc acetate solution and 1 drop of ammonium mercurithiocyanate reagent. If 0.1 γ of copper is present, a violet precipitate will be obtained.

8. **Ammonium Thioacetate** completely precipitates copper sulfide from hot solutions, even in the presence of acid:

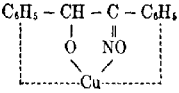
$$C_2H_3OS^- + Cu^{++} + H_2O \rightarrow \mathbf{CuS} + HC_2H_3O_2 + H^+$$

9. **Benzidine** is easily oxidized to a blue, meriquinoidal compound (cf. p. 113), and, in some way, the oxidation takes place when a cupric salt is reduced to the cuprous state by alkali iodide, bromide, cyanide, and thiocyanate. Feigl is inclined to think that the liberated halogen is the cause of the oxidation.

Place successively, on filter paper, 1 drop of the solution to be tested, 1 drop of benzidine reagent, and 1 drop of saturated potassium bromide solution. If 0.6 γ or more of copper is present, a blue spot or ring is formed.

To prepare the reagent, dissolve 1 g of benzidine in 10 ml of acetoacetic ester, dilute the solution with 90 ml of water, shake well, and filter.

10. **α-Benzoinoxime** (cupron), $C_6H_5CHOH-C=NOH \cdot C_6H_5$, forms with copper a green compound which is insoluble in dilute ammonia. According to Feigl the insolubility is caused by the saturation of the secondary valences of copper (shown by the dotted lines) with two phenyl groups:



Place 1 drop of the slightly acid solution to be tested on filter paper, add 1 drop of 5 per cent benzoinoxime in alcohol and evaporate over ammonia. If 0.1 γ of copper is present a green color results. If there is much of an ion present which is precipitated by ammonia, add 1 drop of 10 per cent Rochelle salt solution before adding the cupron.

11. **Catalytic Effect.** The reaction between ferric ions and thiosulfate eventually leads to the formation of ferrous salt and tetrathionate:

$$2\ Fe^{+++} + 2\ S_2O_3^{--} \rightarrow 2\ Fe^{++} + S_4O_6^{--}$$

The reaction takes place in two stages; first a deep violet complex anion $[Fe(S_2O_3)_2]^-$ is formed almost immediately; it is quite stable and decomposes very slowly:

$$[Fe(S_2O_3)_2]^- + Fe^{+++} \rightarrow 2\ Fe^{++} + S_4O_6^{--}$$

The presence of cupric ions catalyzes this second reaction and the violet color fades

much more rapidly than when copper is absent. If the reaction also takes place in the presence of thiocyanate anions, which form a red complex with Fe^{+++} and consequently retard the second stage of the reaction, then, by measuring the time required for complete decolorization, it is possible to detect the presence of as little as 0.02 γ of copper.

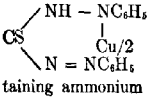
Procedure. — Place, in adjacent cavities on a spot plate, a drop of the solution to be tested and a drop of distilled water. Add to each, 1 drop of reagent prepared by dissolving 1.5 g of ferric chloride and 2 g of potassium thiocyanate in 100 ml of water. Finally add to each 3 drops of 0.1 *N* sodium thiosulfate solution. The color of the blank test will disappear in 1.5 to 2 minutes but if 1 γ of copper is present, the color will disappear almost instantly.

12. **Cupferron** added to an acid solution of a cupric salt precipitates the copper salt of phenylnitrosohydroxylamine,

$$2\,[C_6H_5(NO)NO]^- + Cu^{++} \rightarrow Cu[C_6H_5(NO)NO]_2$$

which dissolves in ammonia giving a blue solution.

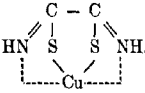
13. **Dithizone** (cf. p. 102) gives a yellowish brown precipitate of



in neutral or ammoniacal solutions and in solutions containing ammonium salts. In the absence of the noble metals and mercury, the test can be obtained with 0.1 γ of copper because the copper has a greater tendency than the other ions to react with the reagent.

In a tiny test tube mix 1 drop of the neutral or slightly ammoniacal solution to be tested with 1 drop of a solution of 1–2 mg of dithizone in 100 ml of carbon tetrachloride. Stopper the tube and shake vigorously. If 0.03 γ of copper is present, the green color of the reagent will become yellowish brown.

14. **Hydrorubianic Acid,** $(CSNH_2)_2$, gives, in ammoniacal and weakly acid solutions containing copper salt, a black precipitate of cupric hydrorubianate,



The precipitation does not take place in potassium cyanide solutions. Cobalt and nickel give brown or blue precipitates with the reagent, but the copper test is so sensitive that it can be carried out in the presence of nickel and cobalt.

Place 1 drop of the carefully neutralized solution to be tested upon filter paper, hold in the fumes of an ammonia bottle, and add 1 drop of a 0.5 per cent solution of the reagent in alcohol. The test has been obtained with as little as 0.006 γ of copper. The reagent, a red crystalline product, is prepared by introducing dry cyanogen (from copper sulfate and an excess of KCN) and hydrogen sulfide into alcohol. Yellow $(CN \cdot CS \cdot NH_2)$ is formed as an intermediate product. After introducing the gases for some time and with an excess of hydrogen sulfide, the red $(CSNH_2)_2$ is eventually obtained. The crystals should be recrystallized from alcohol.

15. **Iron** added to a solution of a copper salt precipitates red, metallic copper:

$$Cu^{++} + Fe \rightarrow Fe^{++} + Cu$$

Other metals, such as zinc, aluminum, etc., which are above copper in the voltage series will give a similar reaction.

The copper may be deposited upon platinum, and thus examined more easily, by

using a strip of platinum foil in contact with zinc, tin, aluminum, etc. In this case an electric couple is formed and the platinum acts as cathode while the other metal, as anode, dissolves.

16. **Phosphomolybdic Acid** gives "molybdenum blue" with potassium cuprocyanide solution. Molybdenum blue is a mixture of molybdenum in different states of oxidation below the valence of six. The molybdenum in phosphomolybdic acid, $H_3Mo_{12}PO_{40}$, is more reactive than that in molybdic acid.

Prepare the reagent by adding ammonium phosphomolybdate (obtained by precipitating alkali phosphate solution with an excess of ammonium molybdate in the presence of hot, dilute nitric acid) to hot aqua regia. Evaporate the solution to dryness on the water bath, take up the residue in water, and recrystallize twice. Keep the dry product in brown bottles. As reagent use a 1 per cent solution in water.

Procedure. — Place in succession upon filter paper 1 drop of the solution to be tested, 1 drop of 1 per cent KCN solution, 1 drop of the phosphomolybdic acid solution, and 1 drop of dilute hydrochloric acid. If the solution contains 1.3 γ of copper a blue coloration will be obtained. The test is less sensitive when large quantities of other ions are present but will be given by 4.0 γ of copper when 300 times as much mercury, 300 times as much lead, 120 times as much bismuth, and 280 times as much cadmium is present. Too much nitric acid is harmful.

17. **Potassium Bromide** solution mixed with concentrated sulfuric acid, and, when cold, covered with a little copper salt solution gives a beautiful bluish red color at the zone of contact of the two solutions. On shaking, the whole solution becomes red. According to Sabatier, the coloration is caused by the formation of

$$CuBr_2 \cdot HBr \cdot 2\,H_2O$$

When considerable copper is present, a black precipitate of copper bromide is obtained. Dilution with water causes the color to disappear. Stannous ions prevent the reaction by reduction of the cupric ions. If sulfur dioxide is added to the dark bluish red solution, a white precipitate of cuprous bromide is obtained.

18. **Potassium Cyanide** produces, at first, yellow cupric cyanide, which immediately loses dicyanogen, forming white cuprous cyanide. The latter, as we have already seen, forms soluble potassium cuprocyanide with more potassium cyanide:

$$2\,Cu^{++} + 4\,CN^- \rightarrow 2\,Cu(CN)_2$$
$$2\,Cu(CN)_2 \rightarrow (CN)_2 \uparrow + Cu_2(CN)_2$$
$$Cu_2(CN)_2 + 6\,(CN)^- \rightarrow [Cu_2(CN)_8]^{----}$$

On adding sufficient potassium cyanide to a blue ammoniacal cupric solution, the complex compound will be decolorized, forming potassium cuprocyanide, and the reduction of the cupric salt to cuprous condition in ammoniacal solution is accomplished at the expense of cyanide ions which are oxidized to cyanate:

$$2[Cu(NH_3)_4]^{++} + 9\,(CN)^- + 2\,OH^- \rightleftarrows [Cu_2(CN)_8]^{----} + (CNO)^- + 8\,NH_3 + H_2O$$

The ratio of simple Cu^+ ions to complex $[Cu_2(CN)_8]^{----}$ ions has been estimated to be as $1 : 10^{28}$ in a normal solution of potassium cyanide.

Hydrogen sulfide will not precipitate cupric sulfide from the colorless solution of potassium cuprocyanide provided sufficient potassium cyanide is present (difference from cadmium). Sometimes, when considerable copper salt is present, the intro-

duction of H_2S causes the formation of a red crystalline precipitate of hydrorubianic acid, $(CSNH_2)_2$. (Cf. p. 135.)

19. **Potassium Ferrocyanide,** $K_4[Fe(CN)_6]$, produces in neutral and acid solutions an amorphous precipitate of reddish brown cupric ferrocyanide,

$$2\,Cu^{++} + [Fe(CN)_6]^{----} \rightarrow \mathbf{Cu_2[Fe(CN)_6]}$$

insoluble in dilute acids, but soluble in ammonia with a blue color (difference from molybdenum ferrocyanide which dissolves in ammonia, forming a yellow solution). It is also decomposed by potassium hydroxide: in the cold, light-blue cupric hydroxide and potassium ferrocyanide are formed; on warming, black cupric oxide is obtained (difference from uranium, which yields the yellow uranate with both ammonia and sodium or potassium hydroxide).

20. **Potassium Iodide** precipitates white cuprous iodide but, owing to the color of the liberated iodine, the precipitate usually appears pink, green, or reddish yellow:

$$2\,Cu^{++} + 4\,I^- \rightarrow \mathbf{Cu_2I_2} + \mathbf{I_2}$$

In the presence of a reducing agent, no free iodine is obtained. In quantitative analysis the copper content is determined by measuring the volume of sodium thiosulfate solution required to react with the iodine:

$$I_2 + 2\,S_2O_3^{--} \rightarrow S_4O_6^{--} + 2\,I^-$$

The cuprous iodide precipitate dissolves in an excess of the reagent. Potassium iodide added to a dilute solution of a cupric salt merely gives a yellow coloration due to the liberated iodine.

21. **Potassium Thiocyanate,** KCNS, precipitates black cupric thiocyanate:

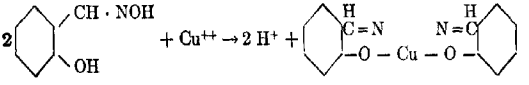
$$Cu^{++} + 2\,(CNS)^- \rightarrow \mathbf{Cu(CNS)_2}$$

which gradually changes into white cuprous thiocyanate, or immediately on adding sulfurous acid:

$$2\,\mathbf{Cu(CNS)_2} + SO_3^{--} + H_2O \rightarrow 2\,CNS^- + SO_4^{--} + 2\,H^+ + \mathbf{Cu_2(CNS)_2}$$

Cuprous thiocyanate is insoluble in water, dilute hydrochloric acid, and dilute sulfuric acid.

22. **Salicylaldoxime,** $C_7H_7O_2N$, in acetic acid solutions gives with cupric ions a light, greenish yellow precipitate of a complex salt, $Cu(C_7H_6O_2N)_2$. Palladium gives a similar precipitate, and gold solutions are reduced to metal by the reagent. These appear to be the only elements that interfere.



Place a drop of the copper solution, which has been neutralized and then made acid with acetic acid, in a tiny test tube and add 1 drop of the reagent. If 0.5 γ of copper is present there will be opalescence, and with more copper a pale green precipitate will form.

To prepare the reagent, dissolve 1 g of salicylaldoxime in 5 ml of alcohol and add the solution dropwise to 95 ml of water at 30°. Shake until the oily suspension almost disappears, and then filter.

23. **Sodium Thiosulfate** decolorizes a neutral or acid solution of a copper salt, and, on boiling the acid solution, a reddish brown precipitate is formed which eventually becomes black cuprous sulfide:

$$2\,Cu^{++} + 2\,S_2O_3^{--} + 2\,H_2O \rightarrow Cu_2S + 4\,H^+ + 2\,SO_4^{--} + S$$

Reactions in the Dry Way

The borax bead or salt of phosphorus bead is green in the oxidizing flame when strongly saturated with the copper salt; blue if containing only a small amount. The reducing flame decolorizes the bead unless too much copper is present; in such a case it is reddish brown and opaque, owing to the separation of copper. Traces of copper may be determined with certainty as follows: To the slightly bluish bead produced by the oxidizing flame, add a trace of tin or of a tin compound. Heat the bead in the oxidizing flame until the tin has completely dissolved, then bring it slowly into the reducing flame and finally quickly remove it. The bead now appears colorless when hot, but ruby-red and transparent when cold. If, however, the bead is kept too long in the reducing flame, it remains colorless; but the ruby-red color may be produced by cautious oxidation. This reaction is very sensitive, and can also be used for the detection of tin.

Heated with charcoal before the blowpipe (or better still with the charcoal stick), spongy metal is obtained.

Copper salts color the flame blue or green. Moistening with hydrochloric acid increases the sensitiveness of this test.

CADMIUM, Cd. At. Wt. 112.41, At. No. 48

Density 8.6. M. P. 321°. B. P. about 766°.

Occurrence. — Cadmium is usually associated with zinc in its ores. It is also found as greenockite, CdS, hexagonal; and as the oxide, CdO,* isometric.

Properties. — The element, discovered by Stromeyer in 1817, derives its name from the Greek word *Kadmia* = earth. It is a silvery white, crystalline metal a little harder than tin or zinc and more tenacious than tin. It is malleable and very ductile. Bending the metal causes it to give a creaking noise, as tin does. It is distinctly volatile above 300°, and in preparing the metal from its ores it is possible

* With smithsonite in the zinc deposits of Monte Poni, Sardinia. *Chem. Ztg.*, **1901**, 561.

to boil off both cadmium and zinc. It forms useful alloys with low melting points, and its sulfide is used in yellow paint. About 3,000,000 pounds of the metal are produced annually.

Cadmium forms but one important oxide, the brownish yellow CdO, which can be obtained by burning the metal in air or by heating the hydroxide, carbonate, nitrate, oxalate, etc. Black cadmium suboxide has been described; it is said to be formed in small quantities when the metal is burned in the air or when cadmium oxalate is heated carefully out of contact with air, but its existence has been questioned, and there are no salts derived from it. Cadmium forms but one series of salts, and in them the cadmium is bivalent. *The best solvent for cadmium is nitric acid.* Dilute hydrochloric and sulfuric acids dissolve it slowly with liberation of hydrogen.

The most important commercial salt is the sulfate, $3\ CdSO_4 \cdot 8\ H_2O$. It is not easily recrystallized. To purify the salt, the concentrated aqueous solution is treated with alcohol, and the crystals that are deposited thereby are filtered, washed with alcohol, and dried upon blotting paper.

Cadmium salts are mostly colorless, though the sulfide is yellow or orange. Most of the salts are insoluble in water, but readily soluble in mineral acids. The chloride, nitrate, and sulfate are soluble in water.

Reactions in the Wet Way

1. **Hydrogen Sulfide** produces precipitates varying in color from a canary-yellow, orange to almost brown, according to the conditions.

In neutral solution, whether hot or cold, light-yellow cadmium sulfide is obtained in a condition hard to filter. From acid solutions (containing in 100 ml from 2 to 10 ml of concentrated H_2SO_4, or from 2 to 5 ml of concentrated HCl) yellow precipitates which turn orange in color are at once thrown down and are easy to filter. These precipitates are not pure CdS, but always contain more or less Cd_2Cl_2S or $Cd_2(SO_4)S$. For this reason cadmium should not be determined quantitatively as the sulfide.

Cadmium sulfide is insoluble in alkaline sulfides (difference from arsenic), but is soluble in considerable hydrochloric acid, warm dilute nitric acid, and hot dilute sulfuric acid (difference from copper). It is also insoluble in potassium cyanide solution (difference from copper).

2. **Alkali** and **Ammonium Carbonates** precipitate the white basic carbonate insoluble in excess. Ammonium salts tend to prevent the precipitation but, on boiling, ammonia gas is evolved and the precipitation is complete. The precipitate dissolves in potassium cyanide solution.

3. **Alkali Hydroxide** precipitates white, amorphous cadmium hydroxide, insoluble in an excess of the reagent (difference from zinc and lead):

$$Cd^{++} + 2\ OH^- \rightarrow Cd(OH)_2$$

On gently igniting the hydroxide the brown oxide is obtained, which

becomes darker on stronger ignition. The ignition of cadmium nitrate yields the black crystalline oxide.

4. **Ammonia** precipitates the white hydroxide, soluble in excess (difference from lead), forming complex tetramminecadmium compounds, as with zinc, nickel, etc.

$$Cd(OH)_2 + 4\,NH_3 \rightarrow [Cd(NH_3)_4]^{++} + 2\,(OH)^-$$

In the presence of normal ammonium hydroxide the ratio of the concentration of the complex anion to that of the simple cadmium cation is about $10^7 : 1$. In pure water, the ionization takes place to a much greater extent; by diluting with water and boiling, cadmium hydroxide is reprecipitated from the solution of the tetramminecadmium compound.

5. **Ammonium Perchlorate** gives a crystalline precipitate of cadmium perchlorate, $Cd(ClO_4)_2$. (Difference from copper.)

6. **Ammonium Sulfide** produces a yellow precipitate of cadmium sulfide, which has a tendency to form colloidal solutions and pass through the filter. The presence of a concentrated salt solution prevents this (cf. p. 131).

7. ***p*-Dinitrodiphenylcarbazide,** $O{=}C\begin{smallmatrix}/NH\cdot NHC_6H_4NO_2\\ \backslash NH\cdot NHC_6H_4NO_2\end{smallmatrix}$, imparts to freshly precipitated cadmium hydroxide a brown coloration which on standing becomes greenish blue. The color is due to adsorption.

Place 1 drop of the acid, neutral, or ammoniacal solution on a spot plate; add 1 drop of 10 per cent sodium hydroxide solution, 1 drop of 10 per cent potassium cyanide solution and 2 drops of 40 per cent formaldehyde solution. If 0.8 γ of cadmium is present, a bluish green coloration is obtained and precipitation takes place with more cadmium. The reagent is red in alkaline solution, but the addition of formaldehyde changes the color to violet. In testing for small quantities of cadmium, therefore, the test should be compared with the color formed in a blank test with pure water. If much copper is present it is necessary to add 3 drops of the potassium cyanide solution and then it requires 4 γ of cadmium to give the test.

8. **Diphenylcarbazide** produces, in neutral or weakly acid solutions which are buffered with alkali acetate a reddish violet precipitate. The reagent diphenylcarbazide, $OC\begin{smallmatrix}/NH\cdot NHC_6H_5\\ \backslash NH\cdot NHC_6H_5\end{smallmatrix}$, is by no means specific for cadmium, but the test for cadmium can be made in the presence of moderate quantities of copper, lead, and mercury.

Prepare a saturated solution of diphenylcarbazide in 90 per cent alcohol, saturate this with solid potassium thiocyanate, and add a crystal of potassium iodide. Moisten some filter paper with the above reagent and dry it. Place on it a drop of the solution to be tested and hold over the fumes of an open ammonia bottle for 1–2 minutes. A bluish violet coloration shows the presence of cadmium. The addition of the thiocyanate and the potassium iodide is to prevent interference of copper, lead, and mercury. If these salts are omitted, the test is given with 4 γ of cadmium; otherwise, with 8 γ.

9. **Metals,** like iron, tin, zinc, etc., do not precipitate cadmium from acid solutions. (Difference from copper.) Zinc precipitates cadmium readily from neutral solutions (see p. 36).

10. **Potassium Cyanide** precipitates white, amorphous cadmium cyanide, readily soluble in excess:

$$Cd^{++} + 2\,(CN)^- \rightarrow \mathbf{Cd(CN)_2}$$
$$\mathbf{Cd(CN)_2} + 2\,(CN)^- \rightarrow [Cd(CN)_4]^{--}$$

From the solution of cadmium potassium cyanide some of the above-mentioned reagents produce no precipitation. In a normal solution of potassium cyanide the concentration of the complex anion to that of the simple cadmium cation is $10^{17} : 1$. This is evidently a much weaker complex than the cuprocyanide anion, and for this reason cadmium sulfide, though its solubility product is much larger than that of cupric sulfide, is precipitated by hydrogen sulfide (difference from copper):

$$[Cd(CN)_4]^{--} + H_2S \rightarrow 2\,CN^- + 2\,HCN + \mathbf{CdS}$$

11. **Potassium Ferrocyanide** gives a white precipitate. (Cf. zinc.)

12. **Potassium Thiocyanate** has no effect upon cadmium solutions. (Difference from copper.)

Reactions in the Dry Way

Cadmium compounds, heated on charcoal with soda, give a brown incrustation of cadmium oxide.

If a compound of cadmium oxide is reduced in the upper reducing flame of the Bunsen burner, the cadmium oxide is changed to metal, which volatilizes, and, in the upper oxidizing flame, goes back to oxide, which will be deposited as a brown coating if a glazed porcelain dish filled with water is held just above the flame. This oxide always contains some suboxide mixed with it, and has the property of reducing silver oxide to metal; so that if the coating of oxide is moistened with silver nitrate solution a black deposit of metallic silver will be obtained:

$$\mathbf{Cd_2O} + 2\,Ag^+ \rightarrow Cd^{++} + \mathbf{CdO} + 2\,\mathbf{Ag}$$

This reaction is very sensitive. If it is desired to test the precipitate produced by hydrogen sulfide for cadmium in this way, first roast the sample in the oxidizing flame and then treat it as just described.

ARSENIC, As. At. Wt. 74.91, At. No. 33

Density 5.7 as metal, yellow 2.0, amorphous 3.69
M. P. 817–18° at 35.8 atm. B. P. about 610°

Occurrence. — Arsenic is widely distributed in nature, being found in small amounts in almost all sulfides, as, for example, sphalerite and pyrites: therefore almost all the zinc and sulfuric acid of commerce contain arsenic.

Properties. — Arsenic occurs native in kidney-shaped masses; also in the form of its dimorphous oxide, As_2O_3, as isometric arsenolite, and monoclinic claudetite. Mimetite, $Pb_5(AsO_4)_3Cl$, hexagonal, isomorphous with apatite, pyromorphite, and vanadinite, is a well-known mineral containing arsenic oxide. The most important sources of arsenic are the sulfides, arsenides, and thio-salts: realgar, As_2S_2, monoclinic; orpiment, As_2S_3, monoclinic; arsenopyrite, FeAsS, orthorhombic; niccolite, NiAs, hexagonal; löllingite, $FeAs_2$, orthorhombic; smaltite, $(Co,Ni,Fe,)As_2$, isometric; and proustite, $As(SAg)_3$, rhombohedral.

Arsenic, which was discovered by Schroeder in 1694 and owes its name to the Greek word *arsenikos* = male, exists in four allotropic forms — metallic, gray, yellow, and brown. When heated in the air, white arsenic trioxide, As_2O_3, is formed. When the metal burns, a strong garlic-like odor prevails which is not noticed when pure arsenic trioxide is sublimed. The vapors are poisonous. In its physical properties arsenic appears to be metallic, but it does not react with the acids containing oxygen so that it is classed with the non-metals. Like phosphorus, the stable arsenic molecule contains four atoms. In this family of the periodic system, the first members, nitrogen and phosphorus, show no basic properties. The lowest members, antimony and bismuth, are distinctly metallic, and their trivalent oxides are distinctly basic. Arsenic, therefore, is the intermediate member of the group.

Arsenic is insoluble in water but is attacked by dry fluorine, chlorine, and bromine, forming compounds of trivalent arsenic. In the presence of water, chlorine and bromine oxidize it first to arsenious and then to arsenic acid:

$$As_4 + 10\ Cl_2 + 16\ H_2O \rightarrow 4\ H_3AsO_4 + 20\ HCl$$

It combines with sulfur to form As_2S_2, As_2S_3, and As_2S_5. It is unattacked by concentrated hydrochloric acid at room temperature but is slowly oxidized by the hot acid to form first arsenic trioxide and then arsenic trichloride:

$$As_4 + (HCl) + 6\ H_2O \rightarrow 2\ As_2O_3 + 6\ H_2\uparrow$$

$$As_2O_3 + 6\ HCl \rightarrow 2\ AsCl_3 + 3\ H_2O$$

Dilute nitric acid dissolves arsenic, forming arsenious acid:

$$As_4 + 4\ HNO_3 + 4\ H_2O \rightarrow 4\ H_3AsO_3 + 4\ NO\uparrow$$

Concentrated nitric acid and aqua regia dissolve it, forming arsenic acid:

$$As_4 + 20\ HNO_3 \rightarrow 4\ H_3AsO_4 + 20\ NO_2\uparrow + 4\ H_2O$$

Sodium hypochlorite solution also dissolves arsenic:

$$10\ NaClO + As_4 + 6\ H_2O \rightarrow 4\ H_3AsO_4 + 10\ NaCl$$

Cold, dilute sulfuric acid is without action, but with hot, concentrated sulfuric acid, arsenious oxide and sulfur dioxide are formed:

$$As_4 + 6\ H_2SO_4 \rightarrow 2\ As_2O_3 + 6\ SO_2\uparrow + 6\ H_2O$$

Arsenic forms two oxides, As_2O_3 and As_2O_5. In reality the formula of the lower oxide is As_4O_6, but it is customary to use the simpler formula, As_2O_3.

A. Arsenious Compounds

Arsenic trioxide is formed by the combustion of arsenic in the air as white, glistening crystals of regular octahedrons. If the vapors of the trioxide are allowed to cool slowly, they solidify to an amorphous glass (arsenic glass), which gradually becomes crystalline (white and opaque, like porcelain).

Arsenic trioxide is known in three different modifications: isometric arsenic trioxide (white arsenic), monoclinic arsenic trioxide, and amorphous, glassy arsenic trioxide.

The monoclinic modification is difficultly soluble in water (80 ml of cold water dissolve 1 g As_2O_3); the amorphous, glassy modification is much more soluble (25 ml of cold water dissolve 1 g arsenic trioxide). The ordinary modification (white arsenic) is not readily wet by water; it floats like flour, and this behavior is very characteristic.

The trioxide dissolves quite readily in hydrochloric acid, particularly on warming, from which solution it often separates out, on cooling, in a beautiful, crystalline, anhydrous condition.

Acting as an acid anhydride it dissolves readily in alkalies, forming easily soluble arsenites:

$$As_2O_3 + 6\ OH^- \rightarrow 3\ H_2O + 2\ AsO_3^{---}$$
$$As_2O_3 + 3\ CO_3^{--} \rightarrow 3\ CO_2\uparrow + 2\ AsO_3^{---}$$

The trimetal arsenites derived from the ortho-acid H_3AsO_3 are usually unstable. Silver arsenite, Ag_3AsO_3, is the only well-known salt of this type. The alkali arsenites are derived from metarsenious acid $HAsO_2$, from pyroarsenious acid $H_4As_2O_5$, or from a polyarsenious acid such as $H_6As_4O_9$. The only salts of sodium and potassium known are of the types $KAsO_2$ and $K_2H_4As_4O_9$; of ammonium, $(NH_4)_4As_2O_5$. In alkaline solution, however, we may assume that AsO_3^{---} ions are present.

Free arsenious acid, H_3AsO_3, has never been isolated; as a very weak acid it breaks down, like carbonic acid, into water and the anhydride.

Arsenic combines with chlorine directly, like phosphorus, forming the chloride, $AsCl_3$, which behaves exactly like the chloride of arsenious acid, similar to PCl_3. It is a colorless liquid, boiling at 134° C, and is decomposed quantitatively, like all acid chlorides, with water:

$$AsCl_3 + 3\ H_2O \rightleftarrows 3\ HCl + H_3AsO_3$$

The aqueous solution of arsenic trichloride and the solution of the trioxide in dilute hydrochloric acid contain the arsenic as arsenious acid. As the concentration of the hydrochloric acid increases, the amount of arsenic trichloride increases, until in very concentrated hydrochloric acid the arsenic is present almost entirely as trichloride. By boiling a solution of arsenic trichloride in hydrochloric acid, arsenic trichloride is driven off as a gas. If hydrochloric acid is conducted into the solution at the same time (so that the concentration of the hydrochloric acid is kept as large as possible), all the arsenic can be volatilized from the solution as arsenious chloride. On evaporating a hydrochloric acid solution of arsenious acid, arsenious chloride constantly escapes, so that all the arsenic may be volatilized. If, however, the arsenic is present in the form of arsenic acid, no arsenic is lost during the evaporation of the solution.

Reactions in the Wet Way

The arsenites of the alkalies are soluble in water; the remaining arsenites are insoluble in water, but soluble in acids.

1. **Hydrogen Sulfide** precipitates from acid solutions yellow, flocculent arsenic trisulfide:

$$2\ H_3AsO_3 + 3\ H_2S \rightarrow 6\ H_2O + As_2S_3$$
$$2\ AsCl_3 + 3\ H_2S \rightarrow 6\ HCl + As_2S_3$$

Arsenious sulfide is insoluble in acids; even boiling 6-normal hydrochloric acid does not dissolve it, but by long boiling with 12-normal hydrochloric acid it is slowly changed to volatile $AsCl_3$ and H_2S. Concentrated nitric acid oxidizes it to arsenic acid and sulfuric acid:

$$As_2S_3 + 28\ HNO_3 \rightarrow 3\ H_2SO_4 + 28\ NO_2\uparrow + 2\ H_3AsO_4 + 8\ H_2O$$

The sulfide dissolves more readily in ammoniacal hydrogen peroxide:

$$As_2S_3 + 14\ H_2O_2 + 12\ OH^- \rightarrow 20\ H_2O + 3\ SO_4^{--} + 2\ AsO_4^{---}$$

It is also dissolved by alkalies, ammonium carbonate, and alkali sulfides:

$$As_2S_3 + 6\ OH^- \rightarrow 3\ H_2O + AsO_3^{---} + AsS_3^{---}$$

$$As_2S_3 + 3\ CO_3^{--} \rightarrow 3\ CO_2\uparrow + AsO_3^{---} + AsS_3^{---}$$

$$As_2S_3 + 3\ S^{--} \rightarrow 2\ AsS_3^{---}$$

Just as the anhydride, As_2O_3, can be referred to the acid, H_3AsO_3, so the thioanhydride, As_2S_3, can be referred to the thioarsenious acid, H_3AsS_3, which is not capable of existence in the free state, but is known in the form of its salts. If one of the latter salts is acidified, then thioarsenious acid is set free; but it immediately loses H_2S, forming the insoluble thioanhydride:

$$2\ AsS_3^{---} + 6\ H^+ \rightarrow 3\ H_2S + As_2S_3$$

On treating a mixture of thioarsenite and arsenite with acid, arsenic trisulfide is also precipitated:

$$AsO_3^{---} + AsS_3^{---} + 6\ H^+ \rightarrow 3\ H_2O + As_2S_3$$

In this last case precipitation is quantitative only when the solution is dilute; from a concentrated solution H_2S escapes, so that more H_2S must be conducted into the solution in order to precipitate all the arsenic.

Boiling a solution of arsenite and thioarsenite with bismuth hydroxide, carbonate or nitrate, etc., results in the formation of black bismuth sulfide:

$$AsS_3^{---} + 2\ Bi(OH)_3 \rightarrow Bi_2S_3 + AsO_3^{---} + 3\ H_2O$$

With cupric oxide, or a soluble copper salt, black cuprous sulfide is formed and the arsenic is oxidized to arsenate:

$$5\ CuO + AsS_3^{---} + AsO_3^{---} \rightarrow 2\ Cu_2S + 2\ AsO_4^{---} + CuS$$

This property of forming thio-salts accounts for the fact that hydrogen sulfide produces no precipitation from normal arsenites, and only a partial precipitation of As_2S_3, from mono- and dimetallic salts:

$$AsO_3^{---} + 3\ H_2S \rightarrow 3\ H_2O + AsS_3^{---}$$

$$6\ HAsO_3^{--} + 15\ H_2S \rightarrow 18\ H_2O + As_2S_3 + 4\ AsS_2^{---}$$

$$3\ H_2AsO_3^- + 6\ H_2S \rightarrow 9\ H_2O + As_2S_3 + AsS_3^{---}$$

Consequently, in order to precipitate arsenic completely as trisulfide, it is always necessary that the solution should contain enough free acid to prevent the formation of soluble thio-salts.

Igniting arsenic trisulfide with sodium carbonate and nitrate causes the formation of sulfate and arsenate:

$$5\,As_2S_3 + 16\,Na_2CO_3 + 28\,NaNO_3 \rightarrow 10\,Na_3AsO_4 + 15\,Na_2SO_4 + 16\,CO_2\uparrow + 14\,N_2\uparrow$$

Heating in a stream of chlorine results in the volatilization of arsenic trichloride. The same reaction takes place when the sulfide is heated in a tube in a current of air with a mixture of five parts ammonium chloride and one of ammonium nitrate.

2. **Ammonium Thioacetate** added to a hot, acid solution of an arsenite produces complete precipitation of arsenic trisulfide:

$$3\,C_2H_3OS^- + 2\,AsO_3^{---} + 9\,H^+ \rightarrow 3\,HC_2H_3O_2 + As_2S_3 + 3\,H_2O$$

3. **Cupric Sulfate** does not precipitate the arsenic from an aqueous solution of arsenious acid; the addition of a little alkali hydroxide causes the formation of yellowish green cupric arsenite, which is soluble in an excess of caustic alkali forming a blue solution, but on boiling red cuprous oxide is precipitated. This is a sensitive reaction for distinguishing arsenious from quinquevalent arsenic compounds, although it must be remembered that many organic reducing agents precipitate cuprous oxide under similar conditions.

4. **Iodine Solution** is decolorized by arsenious acid, which is oxidized to arsenic acid:

$$H_2AsO_3^- + I_2 + H_2O \rightleftarrows 2\,H^+ + 2\,I^- + H_2AsO_4^-$$

To make the reaction take place quantitatively in the direction left to right it is necessary to keep the solution neutral; to make the reaction take place quantitatively in the direction right to left it is necessary to add a considerable excess of hydrogen ions. This is in strict accord with the mass-action principle. This behavior has been explained by assuming that free hydriodic acid is a better reducing agent than iodide ions, but it is more probable that the effect of the acid upon the stability of the arsenic compounds is more important. In alkaline solutions, the arsenic is more stable in the higher state of oxidation, and, for this reason, the arsenite solutions have strong reducing powers in neutral or alkaline solutions. Arsenious acid is amphoteric and forms, as we have seen, a trichloride and trisulfide. In the presence of an excess of hydrogen ions from some other source, arsenious acid will not ionize appreciably as an acid and the tendency will be to form As^{+++} cations. Probably arsenic acid is also amphoteric, though to a much less extent. In strongly acid solutions, the ionization of the arsenic acid is somewhat repressed, and there is a tendency to form As^{+++++} cations, but these are far less stable than As^{+++} cations and, therefore, in strongly acid solutions an arsenate acts as a vigorous oxidizing agent.

The explanation is in line with the results obtained in the study of reduction potentials (cf. p. 46). The addition of acid decidedly increases the oxidizing power of arsenic acid, but slightly diminishes the reduction power of an iodide.

To keep the solution neutral when it is desired to oxidize an arsenite by means of iodine, it is not advisable to use caustic alkali solution, as this itself reacts with iodine, forming iodide and hypoiodite. Sodium bicarbonate is generally used:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2\uparrow$$

Equally satisfactory is sodium phosphate, which forms with hydrogen ions the very

slightly ionized $H_2PO_4^-$ ions. A normal alkali carbonate can be used if the solution is saturated with carbonic acid; there are then not enough OH^- ions formed by the hydrolysis of the normal carbonate to react with the iodine.

5. **Magnesium Chloride** produces no precipitation in dilute arsenite solutions in the presence of ammonia and ammonium chloride (difference from arsenic acid).

6. **Potassium Iodide** added to a hot, acid solution forms red arsenious iodide:

$$AsO_3^{---} + 6\ H^+ + 3\ I^- \rightarrow \mathbf{AsI_3} + 3\ H_2O$$

In concentrated solution, a red precipitate is obtained.

Often, in quantitative analysis, an arsenate is reduced to arsenite by treating the acid solution with a moderate excess of potassium iodide:

$$AsO_4^{---} + 2\ I^- + 2\ H^+ \rightarrow AsO_3^{---} + H_2O + I_2$$

This causes the liberation of red iodine and, if this is boiled off, the color of arsenic tri-iodide appears when the solution is concentrated. In fact, it is difficult to tell when the iodine is all gone and practically impossible to distil off the last traces of iodine without losing some arsenic iodide.

7. **Sodium Thiosulfate** also causes complete precipitation of the arsenic:

$$3\ S_2O_3^{--} + 2\ AsO_3^{---} + 6\ H^+ \rightarrow \mathbf{As_2S_3} + 3\ SO_4^{--} + 3\ H_2O$$

8. **Silver Nitrate** produces in neutral solutions of arsenites a *yellow* precipitate of silver orthoarsenite (difference from arsenic acid):

$$AsO_3^{---} + 3\ Ag^+ \rightarrow \mathbf{Ag_3AsO_3}$$

soluble in nitric acid and ammonia:

$$\mathbf{Ag_3AsO_3} + 3\ H^+ \rightarrow 3\ Ag^+ + H_3AsO_3$$

$$\mathbf{Ag_3AsO_3} + 6\ NH_3 \rightarrow 3\ Ag(NH_3)_2^+ + AsO_3^{---}$$

The first reaction is caused by the formation of non-ionized arsenious acid, which, in the presence of an excess of H^+ ions, furnishes even less AsO_3^{---} ions than are formed by the very slightly soluble Ag_3AsO_3 in contact with water. The solubility in ammonia is due to the fact that the $[Ag(NH_3)_2]^+$ ion in the presence of an excess of NH_3 furnishes fewer simple Ag^+ cations than Ag_3AsO_3 in contact with water.

In aqueous solutions of the mono- and dimetallic salts the precipitation is incomplete:

$$3\ KH_2AsO_3 + 3\ AgNO_3 \rightarrow 3\ KNO_3 + 2\ H_3AsO_3 + \mathbf{Ag_3AsO_3}$$

$$H_2AsO_3^- + 3\ Ag^+ \rightleftarrows \mathbf{Ag_3AsO_3} + 2\ H^+$$

In order to make the precipitation quantitative, a base (preferably ammonia) must be added. As, however, the solution already reacts alkaline, it is difficult to reach the exact neutral point. Usually too much ammonia is added. As a rule in

qualitative analysis it is unnecessary to accomplish complete precipitation in this test, as the *color* of the silver precipitate suffices to show whether an *arsenite* or an *arsenate* is present. To make the precipitation practically complete, add ammonia drop by drop to a solution of silver nitrate until the precipitate of silver oxide that first forms redissolves; the solution then contains complex $[Ag(NH_3)_2]^+$ cations instead of simple Ag^+ ions. Add this reagent to the arsenite solution which has been made weakly acid with nitric acid:

$$H_3AsO_3 + 3\ [Ag(NH_3)_2]^+ + 3\ H^+ \rightarrow 6\ NH_4^+ + Ag_3AsO_3$$

The addition of the nitric acid is necessary, as otherwise the solution will become ammoniacal, dissolving a part of the silver arsenite.

If the solution to be tested contains also a chloride, it should be acidified with nitric acid and the chloride precipitated as silver chloride by an excess of silver nitrate, and filtered off. To the filtrate, dilute ammonia should be added cautiously. At the neutral zone formed by the ammonia above the acid solution, a yellow precipitate of silver arsenite will appear. This test is very sensitive.

9. **Stannous Chloride (Bettendorff's Test).** — On adding to concentrated hydrochloric acid a few drops of an arsenite solution and then $\frac{1}{2}$ ml of a saturated solution of stannous chloride in hydrochloric acid, the solution quickly becomes brown and then black, owing to the deposition of metallic arsenic. The reaction takes place more readily on warming, but a dilute aqueous solution will not give the reaction. In concentrated hydrochloric acid, however, all the arsenic is present as trichloride, and this is reduced by the stannous chloride, whereas arsenious acid is not:

$$2\ As^{+++} + 3\ Sn^{++} \rightarrow 3\ Sn^{++++} + 2\ As$$

B. Compounds of Arsenic Pentoxide

Arsenic pentoxide, which may be obtained by heating arsenic acid, is a white, fusible substance, and is changed by strong ignition into arsenic trioxide:

$$As_2O_5 \rightarrow As_2O_3 + O_2\uparrow$$

Arsenic pentoxide is quite soluble in water, forming arsenic acid:

$$As_2O_5 + 3\ H_2O \rightarrow 2\ H_3AsO_4$$

Arsenic acid itself may be obtained in the solid state in the from of orthorhombic prisms corresponding to the formula $2\ H_3AsO_4 \cdot H_2O$. At 100° C water escapes, orthoarsenic acid, H_3AsO_4, being left behind as a crystalline powder.

By gentle ignition more water is given off, forming pyroarsenic acid, $H_4As_2O_7$, which on further ignition is changed to metarsenic acid, $HAsO_3$. In this respect arsenic acid acts exactly like phosphoric acid. Both the pyro- and the meta-acids readily take on water and are changed back to the ortho acid.

The salts of arsenic acid are called arsenates.

As with orthophosphoric acid, mono-, di-, and trimetallic salts are known: NaH_2AsO_4, Na_2HAsO_4, and Na_3AsO_4.

The arsenates of the alkalies are soluble in water; the others are insoluble in water but easily soluble in acids.

Reactions in the Wet Way

1. **Hydrogen Sulfide** on being passed into a cold solution of an arsenate in 0.3-normal acid does not cause any precipitation until after a long time, when arsenic trisulfide is formed. If the *cold* solution contains a *large excess* of concentrated *hydrochloric acid,* the arsenic is precipitated as pentasulfide. If hydrogen sulfide is passed into a hot solution of an arsenate in concentrated hydrochloric acid, a mixture of arsenic trisulfide and pentasulfide is formed.

This behavior is very interesting, but the relations involved are quite complicated. The solubility products of both arsenic trisulfide and arsenic pentasulfide are extremely small, and it requires but a small quantity of either As^{+++} or As^{+++++} ions to reach this value even with the sulfur ions from slightly ionized hydrogen sulfide. A cold solution of an arsenate in 0.3-normal hydrochloric acid contains no appreciable quantity of As^{+++++} cations. Arsenic acid is of approximately the same strength as phosphoric acid, and it is only in the presence of a very large excess of an acid, such as hydrochloric acid, that the ionization of the first hydrogen acid is repressed to a marked degree. In the presence of concentrated hydrochloric acid, however, it is reasonable to assume that a small quantity of As^{+++++} cations are present. These react with hydrogen sulfide to form the very insoluble pentasulfide,

$$H_3AsO_4 + 5\ H^+ \rightarrow 4\ H_2O + As^{+++++};\ 2\ As^{+++++} + 5\ H_2S \rightarrow \mathbf{As_2S_5} + 10\ H^+$$

The arsenic sulfide is so insoluble that the effect of the acid is, on the whole, favorable; it favors the formation of As^{+++++} cations, and it prevents the formation of colloidal solutions of As_2S_5.

Hydrogen sulfide is absorbed by a cold solution of an arsenate in dilute acid to a greater extent than can be accounted for by the solubility of hydrogen sulfide in water. Soluble thioarsenates are formed:

$$H_3AsO_4 + H_2S \rightarrow H_3AsO_3S + H_2O$$

Hydrogen sulfide also exerts a reducing effect upon the arsenate. This reduction takes place very slowly in the cold, but more rapidly if the temperature of the solution is raised or if the concentration of the H^+ is increased (cf. p. 46):

$$H_3AsO_4 + 3\ H^+ + H_2S \rightarrow As^{+++} + 4\ H_2O + S;\ 2\ As^{+++} + 3\ H_2S \rightarrow \mathbf{As_2S_3} + 6\ H^+$$

As soon as the solution contains an appreciable quantity of either As^{+++++} or As^{+++} ions, the precipitation of the corresponding sulfide at once takes place. The temperature of the solution and the concentration of the acid are exceedingly important factors in the precipitation of arsenic by means of hydrogen sulfide. The pentasulfide is the more insoluble of the two sulfides.

To precipitate the arsenic quickly by hydrogen sulfide from a solution of an arsenate, without employing considerable hydrochloric acid, it is only necessary to reduce the arsenic acid by boiling with sulfurous acid, to boil off the excess of the latter, and then to conduct hydrogen sulfide into the solution, whereby a precipitate of arsenious sulfide is at once formed.

Arsenic pentasulfide is insoluble in boiling concentrated hydrochloric acid, but, like the trisulfide, it is readily soluble in alkalies, ammonium carbonate, and alkali

sulfides:

$$As_2S_5 + 6\ OH^- \rightarrow 3\ H_2O + AsS_4^{---} + AsO_3S^{---}$$
$$As_2S_5 + 3\ CO_3^{--} \rightarrow 3\ CO_2\uparrow + AsS_4^{---} + AsO_3S^{---}$$
$$As_2S_5 + 3\ S^{--} \rightarrow 2\ AsS_4^{---}$$

By acidifying these solutions, arsenic pentasulfide is reprecipitated:

$$2\ AsS_4^{---} + 6\ H^+ \rightarrow 3\ H_2S\uparrow + As_2S_5$$
$$AsS_4^{---} + AsO_3S^{---} + 6\ H^+ \rightarrow 3\ H_2O + As_2S_5$$

Arsenic pentasulfide is oxidized by fuming nitric acid to sulfuric and arsenic acids; also by ammoniacal hydrogen peroxide and by hydrochloric acid and potassium chlorate:

$$As_2S_5 + 40\ HNO_3 \rightarrow 2\ H_3AsO_4 + 5\ H_2SO_4 + 40\ NO_2\uparrow + 12\ H_2O$$
$$As_2S_5 + 20\ H_2O_2 + 16\ OH^- \rightarrow 28\ H_2O + 5\ SO_4^{--} + 2\ AsO_4^{---}$$
$$3\ As_2S_5 + 20\ HClO_3 + 24\ H_2O \rightarrow 20\ HCl + 6\ H_3AsO_4 + 15\ H_2SO_4$$

or

$$3\ As_2S_5 + 5\ HClO_3 + 9\ H_2O \rightarrow 5\ HCl + 6\ H_3AsO_4 + 15\ S$$

2. **Ammonium Molybdate,** added in considerable excess to a boiling nitric acid solution, precipitates yellow, crystalline ammonium arsenomolybdate: $AsO_4^{---} + 3\ NH_4^+ + 12\ MoO_4^{--} + 24\ H^+ \rightarrow 12\ H_2O + \mathbf{(NH_4)_3AsO_4 \cdot 12\ MoO_3}$

This precipitate, like that of the corresponding molybdenum compound with phosphoric acid, is insoluble in dilute nitric acid solution containing ammonium nitrate, but is readily soluble in ammonia or caustic alkali solutions: $\mathbf{(NH_4)_3AsO_4 \cdot 12\ MoO_3} + 24\ OH^- \rightarrow 12\ H_2O + 3\ NH_4^+ + AsO_4^{+++} + 12\ MoO_4^{--}$

The yellow precipitate is also soluble in a solution containing an alkali arsenate; complex anions containing more arsenic are formed and the ammonium salts of these complex ions are soluble in nitric acid. Consequently a large excess of ammonium molybdate should be used if it is desired to precipitate arsenic acid.

As we shall see later, phosphoric acid behaves similarly toward magnesium salts and ammonium molybdate. If, therefore, both phosphoric and arsenic acids are present, it is necessary to precipitate first the arsenic with hydrogen sulfide, filter, and oxidize the precipitated arsenic sulfide to arsenic acid with fuming nitric acid. In such a solution a precipitate produced by means of ammonium molybdate or magnesium chloride must be caused by arsenic acid. In the same way a precipitate produced *in the filtrate* from the hydrogen sulfide precipitate must be caused by phosphoric acid. This is safer than to depend upon the fact that the ammonium phosphomolybdate forms more readily at lower temperatures (60°) than does the corresponding arsenic compound.

3. **Ammonium Thioacetate** and **Sodium Thiosulfate** cause the same precipitation as with arsenious salts.

4. **Concentrated Hydrochloric Acid** and **Ferrous Chloride** cause the formation of volatile arsenious chloride:

$$H_3AsO_4 + 2\,FeCl_2 + 5\,HCl \rightarrow AsCl_3\uparrow + 2\,FeCl_3 + 4\,H_2O$$

Any other soluble ferrous salt may be used or other reducing agents such as cuprous chloride, potassium iodide, potassium bromide, or even hydrogen sulfide. After this treatment, all the arsenic may be removed by distilling in a stream of hydrogen chloride.

Instead of hydrochloric acid, **hydrobromic acid** can be used, and since this acid is a reducing agent no other reducer is required. If, therefore, about 1 g of solid substance is boiled with 10 ml of 9 *N* HBr, practically all the arsenic will be distilled off as $AsBr_3$ if the solution is distilled until only 3 ml remain. By catching the distillate in bromine water a solution of H_3AsO_4 is obtained:

$$AsBr_3 + Br_2 + 4\,H_2O \rightarrow H_3AsO_4 + 5\,HBr$$

Selenium and gallium are also volatilized as $SeBr_3$ and $GaBr_3$ under these conditions.

5. **Cupric Sulfate** does not give a precipitate with arsenic acid solutions unless a little alkali hydroxide is added and then bluish green cupric arsenate is formed which becomes a beautiful light blue on adding more alkali but does not dissolve.

6. **Magnesium Chloride** precipitates, in the presence of ammonia and ammonium chloride, a white, crystalline precipitate of magnesium ammonium arsenate:

$$AsO_4^{---} + Mg^{++} + NH_4^+ \rightarrow \mathbf{MgNH_4AsO_4}$$

This precipitate is insoluble in dilute ammonia and is used for the quantitative determination of arsenic. By ignition it is changed into magnesium pyroarsenate:

$$2\,\mathbf{MgNH_4AsO_4} \rightarrow H_2O\uparrow + 2\,NH_3\uparrow + \mathbf{Mg_2As_2O_7}$$

7. **Potassium Iodide,** in a solution strongly acid with hydrochloric acid, reduces a solution of an arsenate with liberation of iodine (cf. p. 145):

$$H_3AsO_4 + 5\,H^+ + 2\,I^- \rightarrow As^{+++} + 4\,H_2O + I_2$$

The reaction takes place quantitatively if the iodine is removed by adding sodium thiosulfate but, in the absence of acid and the presence of excess $NaHCO_3$, it will take place quantitatively in the reverse direction.

8. **Silver Nitrate** precipitates from neutral solutions *chocolate-brown* silver arsenate (difference from arsenious and phosphoric acids):

$$AsO_4^{---} + 3\,Ag^+ \rightarrow \mathbf{Ag_3AsO_4}$$

soluble in acids and in ammonia.

SPECIAL PROCEDURES FOR ARSENIC

I. The Marsh Test

All compounds containing arsenic can be reduced, in acid solution, by means of metallic zinc to arsine, AsH_3:

$$AsO_3^{---} + 3\ Zn + 9\ H^+ \rightarrow 3\ Zn^{++} + 3\ H_2O + AsH_3\uparrow$$
$$AsO_4^{---} + 4\ Zn + 11\ H^+ \rightarrow 4\ Zn^{++} + 4\ H_2O + AsH_3\uparrow$$
$$As^{+++} + 3\ Zn + 3\ H^+ \rightarrow 3\ Zn^{++} + AsH_3\uparrow$$

The sulfides are reduced very slowly, but the oxides are reduced quickly even at ordinary temperatures.

This *very* poisonous arsine possesses a property which enables us to detect with certainty the merest trace of arsenic — as little as 0.0007 mg As. By conducting the gas through a heated glass tube filled with hydrogen, it is decomposed into hydrogen and metallic arsenic; and the latter is deposited as a brownish black mirror on the sides of the glass tube, just beyond the place where it was heated.

This test is extremely sensitive, and must be made with caution, since almost all reagents, especially commercial zinc and sulfuric acid, are likely to contain traces of arsenic. If these are used without previous testing, arsenic is likely to be found even although it may not have been present in the substance itself.

The Marsh test is particularly useful for detecting the presence of very small amounts of arsenic which could not be found by any of the previously mentioned reactions. In cases of poisoning and for detecting the presence of arsenic in wall-papers, this test, or a modification of it, is always used; we will, therefore, discuss it in detail.

Formation and Properties of Arsine

(*a*) *Formation.* — Arsine is produced, as above mentioned, by the reduction of compounds containing arsenic. For accomplishing the reduction, pure zinc and pure sulfuric acid should be used. If other metals and other acids are used (*e.g.*, tin and hydrochloric acid, iron and sulfuric acid) the arsenic compound will be reduced; but if iron is used, a part of the arsenic is said to be changed to a solid arsenic hydride, which remains in the flask and consequently escapes detection. If tin and hydrochloric acid are used, a high temperature is necessary in order to accomplish the reduction,* but with zinc and sulfuric acid the reaction takes place readily at ordinary temperatures. Chemically pure zinc dissolves with difficulty in chemically pure sulfuric acid, so that it is well to activate the zinc by the addition of a little foreign metal. The addition of a drop of chloroplatinic acid causes at first a more rapid evolution of hydrogen, but the reaction soon slows down and is not accelerated by the addition of more chloroplatinic acid. Moreover, the addition of chloroplatinic acid has the disadvantage of causing considerable arsenic to be held back by the platinum; less than 0.005 mg of As_2O_3 cannot be detected in this way.† Much better results are obtained by using an alloy of zinc and platinum. Thus F. Hefti‡ found that zinc alloyed with 10 per cent platinum caused a more uniform evolution of hydrogen

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* Thus Vanino, working at ordinary temperatures, could not detect less than 0.002 g of As_2O_3 by means of tin and hydrochloric acid, and where chloroplatinic acid was added, less than 0.1 mg of As_2O_3 could not be found. *Z. angew. Chem.*, **1902**, 82.

† Bernstein, Inaug.-Dissert., Rostock, 1870.

‡ Inaug.-Dissert., Zurich, 1907.

and that the formation of arsine was accelerated, while less arsenic was retained by the platinum. With this alloy, 0.0005 mg of As_2O_3 can be detected with certainty. The best activating agent, however, is copper in the form of a zinc-copper alloy prepared as follows: Melt 20 g of the purest zinc in a small Hessian crucible; stir a very little pure copper into the molten zinc with the aid of a stick of zinc. Pour the molten metal into water, keeping as much as possible of the oxide back in the crucible. With this alloy and 15 per cent sulfuric acid, a steady, continuous current of gas is obtained and it is possible to detect with certainty as little as 0.00025 mg of As_2O_3.

Arsenic, arsenious oxide, arsenic pentoxide, and arsenic trisulfide are readily reduced in alkaline solution by sodium amalgam, aluminum, or Devarda's alloy and caustic potash. The reduction takes place quickly, and the arsine may be detected by the Gutzeit reaction (cf. p. 155). The presence of organic matter in solution hinders the reaction; 3 ml of urine in which 1 mg of As_2O_3 was dissolved showed no trace of arsine after treating for hours with Devarda's alloy and caustic potash solution. In such cases the organic substance must be decomposed before testing for arsenic. (Cf. p. 157.)

Arsine is also obtained by dissolving many arsenides in hydrochloric or sulfuric acid:

$$Zn_3As_2 + 6\ HCl \rightarrow 3\ ZnCl_2 + 2\ AsH_3\uparrow$$

Arsenide of iron is attacked by acids only with difficulty, except when an excess of iron is present; solid and gaseous arsenic hydrides are formed. Consequently iron sulfide containing arsenic, on treatment with acids, always yields hydrogen sulfide contaminated with arsine.*

Arsenites can also be reduced to arsine by the action of the electric current. It is possible to distinguish between an arsenite and an arsenate in this way.

Certain molds, namely, *Penicillium brevicaule*, when provided with nutriment containing only traces of arsenic, have the power of forming a volatile arsenic compound having a garlic-like odor; this may be used as an extremely sensitive test for arsenic.

(*b*) *Properties.* — Arsine is a colorless, unpleasant-smelling, extremely poisonous gas, which, on being heated away from the air, is decomposed into arsenic and hydrogen:

$$4\ AsH_3 \rightarrow As_4 + 6\ H_2$$

By heating in the air, it is oxidized to water and arsenic trioxide. Solid iodine changes it to arsenious iodide and hydriodic acid:

$$AsH_3 + 3\ I_2 \rightarrow AsI_3 + 3\ HI$$

This reaction takes place on conducting arsine over solid iodine. *This property serves to free hydrogen sulfide from arsine,* as hydrogen sulfide does not act upon solid iodine, but only upon aqueous iodine solutions. Arsine is not attacked by hydrogen sulfide at ordinary temperatures, but at 230° C sulfide of arsenic and hydrogen are formed.

Arsine is a strong reducing agent: it can reduce silver salts to the metal (see p. 155).

Directions for Performing the Berzelius-Marsh Test

The apparatus devised by G. Lockemann,† shown in Fig. 12, may be used to advantage.

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* *Chem. Zentralbl.*, **1902**, I, p. 1245.

† *Z. angew. Chem.*, **1905**, pp. 427 and 491.

In the flask K, of 100 to 150 ml capacity, place 3 or 4 g of zinc alloyed with copper (cf. p. 152) and about 20 ml of 4-normal sulfuric acid free from arsenic. A steady stream of hydrogen is at once evolved, and in twenty minutes the air will be entirely driven out of the apparatus. When, at the end of about twenty minutes, the gas escaping at b is found to be pure (by collecting a little in a small tube and holding it near a flame; it should light without a sharp explosion), light the hydrogen at b.* The flame should be about 2 or 3 mm high and should remain so during the entire experiment; if it becomes higher, cool the solution in K by placing the flask in cold water, and, conversely, if the flame is too low add a little more sulfuric acid or place the flask in warm water.

First of all, test the zinc and sulfuric acid to see that they are free from arsenic. Heat the hard-glass tube at B just before the constriction in the tube, which is 5 mm long and 1.5–2 mm wide. If at the end of twenty minutes there is no arsenic mirror formed in this capillary, the reagents are free from arsenic.

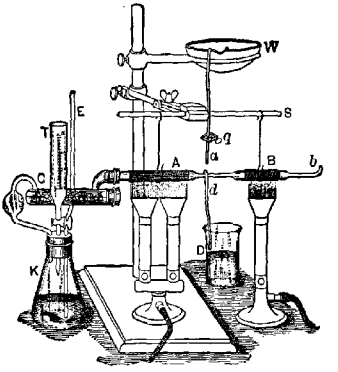


FIG. 12

Transfer the sulfuric acid solution to be tested for arsenic, and which must be free from organic substances, sulfides, chlorides, nitrates, or other oxidizing agents, to the graduated funnel T, and add it little by little to the flask K without in any way interrupting the current of hydrogen. Just before adding the solution to the flask, light the two burners at A and thereby heat the glass tube to dull redness. The gas as it escapes from the flask K passes through the drying-tube C containing granular calcium chloride, and then into the tube A, where any arsine is quantitatively decomposed into arsenic and hydrogen. The arsenic is deposited on the cold walls of the capillary. Cool the end of the capillary, in order to form a sharply defined mirror, by winding around it a piece of wicking, as shown in Fig. 12, and allowing water to drop upon it from the dish W during the experiment.

All the arsenic will be deposited at the end of an hour, and by comparing the mirror with a series of standards the amount can be estimated accurately (see p. 154).

Remark. — If the tube A is not heated at all, but the gas ignited at b as above described, the arsenic may be deposited upon a cold porcelain dish by holding the dish in the flame. The deposit is readily soluble in sodium hypochlorite solution (difference from antimony). In this form the test was used by James Marsh in 1836.

Confirmatory Test. — In the small glass tube open at both ends (see Fig. 13) the arsenic mirror is found. Hold the tube in an inclined position and heat it by means of a small flame whereby the arsenic is changed to arsenic trioxide, giving off the

* A safe way to light the flame is to fill a small tube with the escaping gas, light it, and bring it slowly to the end of the tube b. If the gas is pure the hydrogen in the small tube will burn quietly for some little time. If impure, there will be none left in the small tube after it is exploded and this will not light the escaping gas at b.

characteristic garlic-like odor, which can be detected at the upper end of the tube if only 0.01 mg of arsenic trioxide is formed. After the tube is cooled, the arsenic trioxide is to be found at *a* in the form of small glistening octahedrons, which can be seen with the magnifying glass or often with the naked eye.

These three facts — formation of the mirror, the garlic-like odor, and the octahedrons — suffice to prove the presence of arsenic; but the more proofs we have, the more certain we are of the accuracy of the result. If the octahedrons have been recognized, seal the capillary end of the tube with a flame, and introduce 1 to 2 drops of pure, concentrated hydrochloric acid into the tube with the help of a dropper, and move the tube so that the arsenic trioxide is moistened by the acid; then add 6 to 10 drops of distilled water and pass hydrogen sulfide into the tube, whereby yellow arsenious sulfide is formed.

The hydrogen sulfide required may be generated from a solution of sodium sulfide by allowing it to flow into dilute sulfuric acid, as

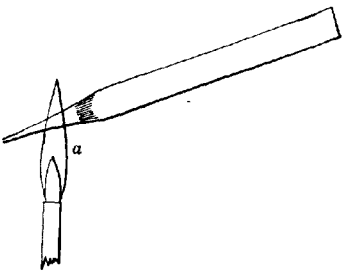


FIG. 13

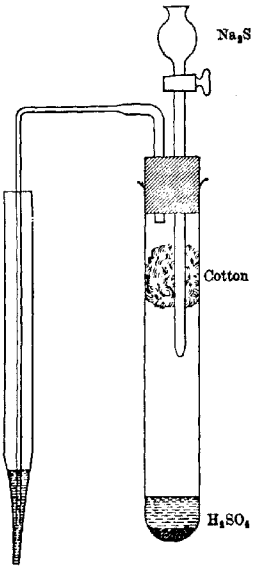


FIG. 14

illustrated in Fig. 14. The upper part of the test tube contains a wad of cotton wool, which prevents any of the solution in the tube from being mechanically carried over into the tube containing the arsenic.

As an example of the practical application of this delicate test, the method to be employed in the detection of arsenic in wall-papers, etc., will be described. The amount of arsenic contained in wall-papers is usually so small that weighing the mirror produced would not be accurate.* It is best, therefore, to prepare a number of mirrors from known amounts of arsenic, to establish a scale for determining how much is contained in the given wall-paper or fabric.†

First of all, the arsenic must be extracted completely from the paper, and to this end it is necessary to decompose the organic material.

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* In Massachusetts, the law permits the presence of 0.1 mg per square decimeter in wall-paper, but only 0.01 mg per square decimeter in wearing apparel. In most cases it is merely necessary to determine whether the legal limit is exceeded.

† C. R. Sanger, *Am. Acad. Arts Sci.*, **26**, 24.

2. *The Gutzeit Test*

The Gutzeit Test for Arsenic depends upon the behavior of arsine toward a 50 per cent solution of silver nitrate (according to Eidenbenz, a crystal of solid silver nitrate should be used). The silver nitrate is at first colored yellow and then black, the following reactions taking place:

$$6\ AgNO_3 + AsH_3 \rightarrow \underbrace{AsAg_3 \cdot 3\ AgNO_3}_{\text{Yellow}} + 3\ HNO_3$$

$$AsAg_3 \cdot 3\ AgNO_3 + 3\ HOH \rightarrow H_3AsO_3 + 3\ HNO_3 + 6\ Ag$$

The test is carried out as follows: Place a little of the substance in a small test tube, Fig. 15, add a few grains of zinc and a little dilute sulfuric acid, and place a wad of cotton near the top of the tube as a filter. Over the mouth of the tube place a piece of filter paper with a crystal of silver nitrate on top.

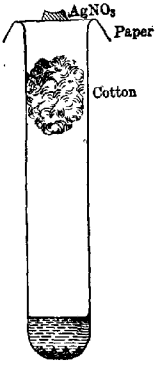


FIG. 15

If arsenic is present, the silver nitrate is at first turned yellow, but it becomes black very quickly.

This reaction is often used for quickly testing commercial acid for arsenic, but it is not as reliable as the Bettendorff test (p. 147), because phosphine* and stibine give a similar reaction with silver nitrate, while they are not reduced by stannous chloride.

If arsine is allowed to act upon a dilute solution of silver nitrate, the yellow compound $AsAg_3 \cdot 3\ AgNO_3$ is not formed, for it is immediately decomposed hydrolytically, according to the equation

$$AsH_3 + 6\ AgNO_3 + 3\ HOH \rightarrow 6\ HNO_3 + H_3AsO_3 + 6\ Ag$$

If the precipitated silver is filtered off, and ammonia then poured on top of the filtrate, the neutral zone will appear yellow owing to the formation of silver arsenite.

This reaction never takes place quite quantitatively; the deposited silver invariably contains a little silver arsenide, Ag_3As.

If the silver solution is made ammoniacal, it is true that all the arsine will be absorbed, but the deposited silver still contains a little arsenic and the solution a small quantity of ammonium arsenite. If, however, the ammoniacal solution containing the silver nitrate and ammonium arsenite is heated to boiling, then the arsenite is oxidized quantitatively to arsenate with deposition of silver.†

$$2\ Ag^+ + AsO_3^{---} + OH^- \rightarrow HAsO_4^{--} + 2\ Ag$$

Under these conditions eight atoms of silver are deposited from each original molecule of arsine

$$AsH_3 + 8\ Ag^+ + 11\ OH^- \rightarrow AsO_4^{---} + 7\ H_2O + 8\ Ag$$

If the deposited silver is filtered off and the filtrate carefully neutralized with nitric acid, a brown precipitate of silver arsenate is formed.

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* Commercial zinc often contains a small quantity of phosphorus.

† Cf. Reckleben, Lockemann, and Eckhardt, *Z. anal. Chem.*, **1907**, 671.

Somewhat less sensitive than the original Gutzeit test, although very satisfactory, is the modification recommended by Flückiger* and Lehmann.†

Instead of allqwing the arsine to act upon silver nitrate, bring it into contact with mercuric chloride paper‡, which is turned yellow by a little arsine and reddish brown by considerable arsine.§

The exact composition of these compounds is not known definitely. Possibly $As(HgCl)_3$ is formed first; and then, by further action of AsH_3, $AsH(HgCl)_2$ and As_2Hg_3 are formed.‖

$$AsH_3 + 3\,HgCl_2 \rightarrow 3\,HCl + As(HgCl)_3$$
$$2\,As(HgCl)_3 + AsH_3 \rightarrow 3\,AsH(HgCl)_2$$
$$As(HgCl)_3 + AsH_3 \rightarrow 3\,HCl + As_2Hg_3$$

These arsenic compounds are characterized by their insolubility in 80 per cent alcohol.

Stibine gives no reaction in this test when little of it is present, but the presence of somewhat more of it causes the formation of a brown spot which is soluble in alcohol. If, however, both arsenic and antimony are present, the former is recognized by cutting out the spot from the rest of the filter paper and placing it in 80 per cent alcohol, whereby the brown spot due to the antimony is removed in a short time and the yellow arsenic spot appears plainly. When considerable antimony is present, the test fails; a gray-black spot is produced which does not disappear on treatment with alcohol.

3. The Reinsch Test

The Reinsch Test is very easy to make, but it is not as sensitive as the tests just mentioned. It depends upon the fact that, when a strip of polished copper foil is added to a solution of arsenious acid, the copper is colored gray owing to the deposition of Cu_5As_2 on the copper.

From concentrated solutions the arsenic separates out in the cold, but from dilute solutions only on warming. If considerable arsenic is present, the gray copper arsenide drops off from the copper. Antimony is also precipitated on copper from its solutions, so that the deposit must be tested for arsenic in the dry way. Arsenic acid is also reduced by copper, but only on warming.

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* *Arch. Pharm.* [3], **1889**, 27.

† *Pharm. Ztg. Berlin*, **1892**, 36.

‡ To prepare the mercuric chloride paper moisten some filter paper with an alcoholic solution of mercuric chloride, allow the alcohol to evaporate, and repeat the process four or five times.

§ August Gotthelf, *J. Soc. Chem. Ind.*, **22**, 191 (1903).

‖ Besides the above compounds, $AsH_2(HgCl)$ is said to exist. Cf. Partheil, *Arch. Pharm.*, **237**, 121.

The Reinsch test is often used in testing wall-papers for arsenic. The pieces of paper are treated with a little hydrochloric acid (1 : 2), a piece of copper foil added, and warmed. A gray deposit on the copper indicates the presence of arsenic.

To confirm this test, the piece of gray copper foil is placed in a tube of difficultly fusible glass and heated in a stream of hydrogen gas; an arsenic mirror is produced which can be tested as described on page 153.

Detection of Arsenic in Human Organs

To detect small quantities of arsenic present in the organs of persons who have probably died from poisoning, it is necessary in the first place to destroy all the organic tissue; this may be accomplished by the action of sulfuric and nitric acids.* Place 200 g of the organ, 200 ml of concentrated nitric acid, and 5 ml of 2 per cent permanganate solution in a 2-l flask and heat until foaming ceases. Then transfer the solution to a 1-l flask, rinsing out the larger flask with 100 ml of concentrated nitric acid and 100 ml of water. Boil four hours, or until the solution is reduced to 80 ml in volume. Add 100 ml of concentrated sulfuric acid and evaporate till fumes of sulfuric acid are evolved. Cool, add 2 or 3 ml of concentrated nitric acid, and again heat until white fumes are evolved, and repeat this treatment with nitric acid about six times. Then, when all the nitric acid has been expelled, cool, dilute with 100 ml of water, and test the solution by the Marsh test.

To determine the *quantity* of arsenic present, transfer the solution to a distilling flask, add 20 ml of concentrated sulfuric acid, 50 g of sodium chloride, 1 g of potassium chloride, and 10 g of ferrous sulfate crystals. Distil into a flask containing 50 g of sodium bicarbonate and 100 ml of water until all the solid bicarbonate dissolves. Titrate the sodium arsenite solution thus obtained with iodine as described in Vol. II. A blank experiment should be made with all the reagents to make sure that they are free from arsenic.

Reactions in the Dry Way

Metallic arsenic burns, giving off a garlic-like odor. Mixed with sodium carbonate and heated on charcoal, all arsenic compounds give this odor.

Oxygen compounds of arsenic are easily reduced to metal in the upper reducing flame. If a porcelain dish (glazed on the outside and filled with water) is held directly over the sample, the arsenic vapors are condensed on the dish, forming a brownish black coating which is soluble in sodium hypochlorite solution, disappearing instantly, the arsenic being oxidized to arsenic acid:

$$As_4 + 10\,NaOCl + 6\,H_2O \rightarrow 10\,NaCl + 4\,H_3AsO_4$$

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* Cf. Gautier, *Bull. soc. chim. Paris*, **25**, 252 (1875); Chittenden and Donaldson, *Am. Chem. J.*, **11**, 236 (1880–1); Joachimoglu, *Arch. exptl. Path. Pharmakol.*, **78**, 1–16 (1914).

If the porcelain dish is not held closely above the reducing flame, but above the upper oxidizing flame, the arsenic vapors are burned with a bluish flame to white arsenious oxide which deposits on the dish. If this deposit is moistened with silver nitrate, and ammonia vapors blown upon it, a yellow coloration due to Ag_3AsO_3 is formed, which disappears if more ammonia is allowed to act upon it (difference from antimony):

$$As_2O_3 + 6\,AgNO_3 + 3\,H_2O \rightarrow 2\,Ag_3AsO_3 + 6\,HNO_3$$

The ammonia serves to neutralize the nitric acid formed by the reaction, but the precipitate dissolves in excess of ammonia as well as in nitric acid.

The microchemical method of Hartwich and Toggenburg* is often useful when the arsenic is present as trioxide. Prepare a glass cylinder about 12 mm in diameter and 10 mm in height and make sure that both the upper and lower edges are smooth. Place this cylinder upon a small watch glass and pour into it a little of the substance to be tested, well mixed with ignited sand. Cover the cylinder with a flat glass slide about 50 mm square. Heat the watch glass very carefully with the flame from a small burner; the flame should not be over 5 mm high and 30 to 40 mm below the watch glass. After heating ten or fifteen minutes, allow to cool slowly, and finally examine the bottom surface of the glass slide. If arsenic is present as trioxide, it will have sublimed and the vapors will have condensed, upon the slide for the most part, in the form of beautiful octahedrons, the shape of which is very distinct when viewed under the microscope. These crystals are visible when only 0.01 mg of arsenic is present. The sublimate may be identified further by the silver reaction.

Arsenic trioxide or trisulfide is readily reduced to metallic arsenic by fusion with a mixture of 3 parts sodium carbonate and 1 part potassium cyanide. With the oxide the cyanide is changed to cyanate, but with the sulfide some thiocyanate is formed. The reaction succeeds with arsenites provided the cation is not reduced by potassium cyanide and does not yield an arsenide which is easily decomposed by heating. This reaction is recommended by Fresenius and Babo as most suitable for detecting the presence of small quantities of arsenic. They recommend the following procedure:

Triturate the perfectly dry arsenic compound with 3 times as much dry potassium cyanide and 9 times as much sodium carbonate in a mortar which has been warmed. To avoid contact of the fusion mixture with glass, which is likely to contain arsenic, place the mixture in a small porcelain boat and introduce the boat into a piece of glass tubing which is drawn out into a capillary at one end. Connect the other end of the tubing with a carbon dioxide generator, interposing a wash bottle with a little sulfuric acid to dry the carbon dioxide. The porcelain boat should rest in the middle of the glass tube. With a moderate stream of carbon dioxide passing through the

* *Schweiz. Wochenschrift für Chem. u. Pharm.* **1909**, No. 52, p. 1.

apparatus, heat the whole length of the glass tube to remove all moisture, then shut off the flow of gas somewhat and heat the end of the tube where the constriction begins. When this is hot place another lamp under the porcelain boat and continue heating until all the arsenic is expelled. Most of it will condense in the narrow tubing but some may escape into the air and give a garlic-like odor. As little as 0.01 mg of arsenious acid will produce a visible mirror of arsenic.

ANTIMONY, Sb. At. Wt. 121.76, At. No. 51

Density 6.7. M. P. 630°. B. P. 1440°

Occurrence. — Antimony seldom occurs free in nature, although large amounts of the metal have been found in Australia. The most important compounds containing antimony are (as with arsenic) the sulfur compounds. Stibnite, Sb_2S_3, orthorhombic, is found in Japan in beautiful crystals. The occurrence of kermesite, Sb_2OS_2, is interesting, as this compound is often met with in analysis.

Of the oxygen compounds the dimorphous antimony trioxide is known as isometric senarmontite and orthorhombic valentinite. Antimony also occurs in many thiosalts, of which the tribasic silver thioantimonite, or pyrargyrite, Ag_3SbS_3, may be mentioned.

Properties. — Antimony owes its name to the Latin word *antimonium* and its symbol is from *stibium*. It was discovered about 1450 and Basil Valentine wrote a book about antimony and its compounds. About 24,000 tons are mined annually, and most of it comes from China. Antimony is used chiefly in making alloys, type metal, Babbitt metal, storage battery plates, etc. Its compounds find extensive use. Thus the sulfide, Sb_2S_3, is used as a pigment, and various antimony compounds are used in medicine and in other pharmaceutical products.

Antimony is a silver-white, brittle metal. It burns readily in the air to antimony trioxide. *The proper solvent for antimony is aqua regia*, by which it is converted into the trichloride or pentachloride. Nitric acid attacks antimony, changing it into Sb_2O_4, which dissolves slightly in concentrated acid, but is insoluble in dilute acid. Antimony dissolves easily in a mixture of nitric and tartaric acids, and in a mixture of hydrochloric acid and bromine.

Antimony forms three oxides: antimony trioxide, Sb_2O_3; antimony pentoxide, Sb_2O_5; and antimony tetroxide, Sb_2O_4, which may be regarded as antimonous antimonate, and is a very indifferent substance chemically. Antimony trioxide as a rule shows basic properties; antimony pentoxide has more the character of an acid anhydride.

A. Compounds of Antimony Trioxide

By burning the metal in the air, the trioxide is obtained, which on stronger ignition in the presence of air is changed to the inert Sb_2O_4.

The trioxide is dissolved by concentrated hydrochloric acid, forming antimony trichloride, a compound which (like bismuth chloride) is readily changed into a basic salt by the action of water, the decomposition of which depends upon the concentration of the reacting substances. Thus antimonyl chloride, SbOCl, is known, which is formed according to the following equation:

$$SbCl_3 + H_2O \rightarrow 2\,HCl + SbOCl$$

In the presence of a large amount of water some oxide is also formed:

$$2\,SbOCl + H_2O \rightarrow 2\,HCl + Sb_2O_3$$

A mixture of antimonyl chloride and antimony trioxide is known as "Algaroth" powder, $Sb_2O_3 \cdot 2\,SbOCl$. By boiling with considerable water the oxide alone is obtained.

Antimony trioxide forms three hydroxides, which behave as very weak acids: orthoantimonous acid, H_3SbO_3; pyroantimonous acid, $H_4Sb_2O_5$; and the hypothetical metantimonous acid, $HSbO_2$.

Salts of the metantimonous acid are known, although the free acid itself has never been isolated. On boiling the oxide Sb_2O_3 with concentrated caustic soda or potash, it goes into solution, but on dilution with considerable hot water Sb_2O_3 separates out again. On filtering this off, tetragonal crystals of $NaSbO_2$ are deposited in the filtrate on cooling; they are very unstable, however, and are decomposed by standing in the air into sodium carbonate and antimony trioxide. By dissolving antimony trioxide in strong alkali, the orthoantimonite is probably formed,

$$Sb_2O_3 + 6\,OH^- \rightarrow 2\,SbO_3^{---} + 3\,H_2O$$

which is hydrolyzed on dilution into metantimonite and alkali hydroxide:

$$SbO_3^{---} + H_2O \rightarrow 2\,OH^- + SbO_2^-$$

The latter is decomposed by more water into trioxide and alkali hydroxide, so that, on adding to a solution of the trichloride either sodium hydroxide or carbonate, an almost quantitative precipitation of Sb_2O_3 will be obtained:

$$2\,SbCl_3 + 6\,NaOH \rightarrow 6\,NaCl + 3\,H_2O + Sb_2O_3$$
$$2\,SbCl_3 + 3\,Na_2CO_3 \rightarrow 6\,NaCl + 3\,CO_2\uparrow + Sb_2O_3$$

Antimony oxychloride, SbOCl, contains the univalent group, SbO^+, which is known as the antimonyl group.

Antimony oxychloride, therefore, can be regarded as antimonyl chloride. Antimonyl nitrate, $SbO(NO_3)$, is also known, and antimonyl sulfate, $(SbO)_2SO_4$. All these compounds are easily hydrolyzed into acid and oxide, so that they are rarely encountered in the course of analysis, with the exception of antimonyl chloride.

The antimonyl compounds of certain organic acids (such as tartaric acid) are very much more stable.

On boiling antimony trioxide with a solution of potassium acid tartrate, it dissolves, forming the so-called tartar emetic,

$$2\,KHC_4H_4O_6 + Sb_2O_3 \rightarrow H_2O + 2\,K(SbO)C_4H_4O_6$$

which is comparatively soluble in water: 100 ml of water dissolve 5.3 g at 8.7°; 7.9 g at 21°; 12.2 g at 31°; 18.2 g at 50°; and 31.2 g at 75°.

Not only antimony oxide, Sb_2O_3, but all antimonyl compounds, form a complex anion with tartaric acid or with a tartrate; thus, antimonyl chloride dissolves in Rochelle salt, or in tartaric acid:

$$C_4H_4O_6^{--} + SbOCl \rightarrow Cl^- + [(SbO)C_4H_4O_6]^-$$
$$H_2C_4H_4O_6 + SbOCl \rightarrow HCl + H[(SbO)C_4H_4O_6]$$

Tartar emetic, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}\,H_2O$, is the most important antimony compound of commerce. Consequently it will be worth while to say a few words with regard to its behavior toward acids.

If an aqueous solution of potassium antimonyl tartrate is treated with hydrochloric acid, a white precipitate of antimonyl chloride is formed,

$$K(SbO)C_4H_4O_6 + 2\,H^+ + Cl^- \rightarrow H_2C_4H_4O_6 + K^+ + SbOCl$$

which readily dissolves in more hydrochloric acid,

$$SbOCl + 2\,HCl \rightleftarrows H_2O + SbCl_3$$

but, on the addition of more water, it is reprecipitated, etc.

Sulfuric and nitric acids precipitate orthoantimonous acid from a solution of potassium antimonyl tartrate, for the antimonyl compound, which is at first formed, is immediately decomposed by water:

$$[(SbO)C_4H_4O_6]^- + H^+ + 2\,H_2O \rightarrow H_2C_4H_4O_6 + H_3SbO_3$$

Water added to a solution containing antimony usually precipitates antimonous acid or a basic salt. By boiling a solution of antimony in either state of valence with nitric acid and evaporating nearly to dryness, all the antimony can be precipitated as oxide. If the oxide is filtered off and heated, it corresponds closely to the formula Sb_2O_4, which can be regarded as antimonous antimonate. The presence of tartaric acid tends to prevent the hydrolysis.

Reactions in the Wet Way

1. **Hydrogen Sulfide** precipitates, from solutions which are not too acid, flocculent, orange-red antimony trisulfide:

$$2\,Sb^{+++} + 3\,H_2S \rightarrow 6\,H^+ + Sb_2S_3$$

As is indicated in the equation, the antimony trisulfide is in equilibrium with hydrogen ions; in 12-normal acid it is readily soluble (difference from arsenic). On the other hand, antimony sulfide is less soluble in acid than is tin sulfide and it can be precipitated from a solution which is over twice normal in acid. The lower sulfides of both tin and antimony are somewhat more soluble than the higher sulfides. If a solution of antimony in concentrated hydrochloric acid is to be treated with hydrogen sulfide and the solution is first diluted, a precipitate of SbOCl is likely to form. This does no harm, as hydrogen sulfide will change antimonyl chloride into the less soluble trisulfide. If it is desired to precipitate the sulfide without any formation of antimonyl chloride, the solution should be saturated with hydrogen sulfide before it is diluted, then diluted and again saturated with hydrogen sulfide.

By heating orange antimony sulfide in an inert atmosphere (CO_2) it is changed to black antimony trisulfide. By roasting in the air, antimony tetroxide, Sb_2O_4, is formed. Heated with sodium nitrate, a mixture of sodium sulfate and pyroantimonate is formed. Heated in chlorine, or with a mixture of 5 parts ammonium chloride and 1 part ammonium nitrate, the antimony is changed to chloride which can be volatilized, though less readily than the corresponding arsenic compound.

Antimony trisulfide is soluble in ammonium sulfide, forming a soluble thio-salt: $Sb_2S_3 + 3\,S^{--} \rightarrow 2\,[SbS_3]^{---}$.

The triammonium salt has never been isolated, the mono salt, NH_4SbS_2, alone being known in the solid state. In solution, however, particularly in the presence of considerable ammonium sulfide, the SbS_3^{---} ion is probably present.

If yellow ammonium sulfide is employed, ammonium salts of thio-antimonic acid are obtained:

$$Sb_2S_3 + 2\,(NH_4)_2S_2 \rightarrow (NH_4)_3SbS_4 + NH_4SbS_3$$

If the solution of ammonium thioantimonite is boiled for a long time in the air, the red-colored oxysulfide is often precipitated:

$$2\ (NH_4)_3SbS_3 + 4\ O_2 \rightarrow 2\ (NH_4)_3S_2O_3 + 2\ NH_3\uparrow + H_2O + Sb_2S_2O$$

By boiling antimony chloride with sodium thiosulfate, the oxysulfide is also obtained, $2\ Sb^{+++} + 3\ S_2O_3^{--} \rightarrow 4\ SO_2\uparrow + Sb_2S_2O$, which, on being warmed with ammonium sulfide, redissolves, forming the thio-salt.

Antimony trisulfide is also soluble in caustic alkali, forming thio-and oxythio salts:

$$Sb_2S_3 + 2\ OH^- \rightarrow H_2O + SbOS^- + SbS_2^-$$

These thio-salts are decomposed by acids, precipitating antimony trisulfide, with evolution of hydrogen sulfide:

$$2\ SbS_3^{---} + 6\ H^+ \rightarrow 3\ H_2S\uparrow + Sb_2S_3$$
$$2\ SbS_4^{---} + 6\ H^+ \rightarrow 3\ H_2S\uparrow + Sb_2S_5$$
$$SbOS^- + SbS_2^- + 2\ H^+ \rightarrow H_2O + Sb_2S_3$$

Boiling a solution of antimony trisulfide in potassium hydroxide or alkali sulfide with bismuth oxide results in the formation of insoluble bismuth sulfide and soluble antimonite

$$Bi_2O_3 + SbS_3^{---} \rightarrow Bi_2S_3 + SbO_3^{---}$$

If the alkaline thioantimonite solution is boiled with cupric oxide, insoluble cuprous and cupric sulfides and soluble antimonate are formed:

$$4\ CuO + SbS_3^{---} \rightarrow SbO_4^{---} + Cu_2S + 2\ CuS$$

2. **Alkali Hydroxide, Ammonia,** and **Alkali Carbonates** precipitate the amorphous hydrated oxide.

3. **Ammonium Thioacetate** and **Sodium Thiosulfate** precipitate antimonous sulfide from acid solutions. Under suitable conditions, "antimony cinnabar" Sb_2S_2O, or a mixture of Sb_2S_3 and some Sb_2O_3, is formed with sodium thiosulfate.

4. **Phosphomolybdic Acid** is reduced to "molybdenum blue" by antimony trichloride solution. In systematic qualitative analysis, the sulfides of arsenic, antimony, and tin are dissolved in alkali polysulfide and the addition of acid causes precipitation of As_2S_5, Sb_2S_5, and SnS_2. If the precipitate is treated with 6 *N* hydrochloric acid, the solution contains $SbCl_3$ and $SnCl_4$. In such a solution the following test is specific for antimony:

Place a drop of the solution upon filter paper which has been impregnated with phosphomolybdic acid (see p. 136), and hold the paper in steam. If 0.2 γ of antimony is present, a blue coloration will be obtained.

5. **Potassium Iodide** does not set free iodine when treated with an antimonous solution (difference from antimonic compounds).

6. **Water** often precipitates a basic salt (see p. 161).

7. **Zinc** precipitates metallic antimony from solutions of antimony compounds. If a piece of platinum foil and a little zinc are placed in an antimony solution containing hydrochloric acid, so that the two

metals touch one another, the antimony is deposited on the platinum in the form of a black stain which does not disappear on removal of the zinc (difference from tin).

Lead, tin, and other metals will also cause the same reaction to take place (cf. p. 43). Zinc, however, unlike iron, tin, and lead, is likely to carry the reduction farther, and stibine gas, SbH_3, is formed with a part of the antimony:

$$2\,Sb^{+++} + 3\,Zn \rightarrow 3\,Zn^{++} + 2\,Sb$$
$$Sb^{+++} + 3\,Zn + 3\,H^{+} \rightarrow 3\,Zn^{++} + SbH_3\uparrow$$

The stibine behaves like arsine in the Marsh test, but the antimony is less volatile and less soluble in sodium hypochlorite solution.

B. Compounds of Antimony Pentoxide

Antimony pentoxide, Sb_2O_5, is formed as a yellow powder by oxidizing antimony with concentrated nitric acid and gently igniting the reaction product (antimonic acid). On strong ignition it loses oxygen and goes over into the very stable antimonous antimonate Sb_2O_4.

The pentoxide dissolves in concentrated hydrochloric acid, forming the pentachloride

$$Sb_2O_5 + 10\,HCl \rightarrow 5\,H_2O + 2\,SbCl_5$$

If this solution is treated with water, a white precipitate of antimonic oxychloride, SbO_2Cl, is formed, which, by the addition of more water, is changed on warming into antimonic acid:

$$SbCl_5 + 2\,H_2O \rightleftarrows 4\,HCl + SbO_2Cl$$
$$SbO_2Cl + 2\,HOH \rightleftarrows HCl + H_3SbO_4$$

Tartaric acid prevents the precipitation of the oxychloride, as with SbOCl (p. 160). Antimony pentoxide is an acid anhydride, and, like the corresponding P_2O_5, can be referred to three acids, orthoantimonic acid, H_3SbO_4; metantimonic acid, $HSbO_3$; and pyroantimonic acid, $H_4Sb_2O_7$, all of which have been isolated. The salts of the metantimonic and pyroantimonic acids are the most common. The trimetallic salts of the ortho acid have never been isolated, but the monometallic salts are known to exist. All antimonates, being salts of a weak acid, are very unstable, being easily hydrolyzed by water.

If antimony pentoxide is fused with an excess of caustic potash, the product of the fusion probably contains the trimetallic salt of orthoantimonic acid. If, however, the melt is dissolved in a little water and allowed to crystallize, deliquescent crystals of potassium pyroantimonate, $K_4Sb_2O_7$, are formed.

The ortho salt, which is first formed, is decomposed by water as follows:

$$2\,K_3SbO_4 + H_2O \rightleftarrows 2\,KOH + K_4Sb_2O_7$$

By the action of considerable cold water (or more quickly by rapid boiling with less water) this deliquescent salt is gradually changed into potassium dihydrogen antimonate,

$$K_4Sb_2O_7 + 3\,H_2O \rightleftarrows 2\,KH_2SbO_4 + 2\,KOH$$

which separates out with 3.5 molecules of water as a granular powder, difficultly

soluble in cold water. It dissolves to a considerable extent in water at about 40°–50° C; this solution is used in testing for sodium, as the sodium salt is very much more insoluble in water.

On boiling $K_2H_2Sb_2O_7$ a long time with considerable water, it gradually takes on water, forming the easily soluble monometallic salt of orthoantimonic acid,

$$K_2H_2Sb_2O_7 + H_2O \rightleftarrows 2\ KH_2SbO_4$$

which is obtained, on evaporating the solution, as a gummy mass of the composition $2\ KH_2SbO_4{\cdot}H_2O$, but on boiling the aqueous solution for a long time, more KOH is lost, with the formation of amorphous orthoantimonic acid:

$$KH_2SbO_4 + H_2O \rightleftarrows KOH + H_3SbO_4$$

All antimonates are decomposed by acids, amorphous antimonic acid separating out.

The gummy, monometallic salts give an amorphous precipitation with sodium salts, gradually becoming crystalline, while the potassium dihydrogen antimonate gives a crystalline precipitate immediately.

The relations of antimonous to antimonic acids and of antimonites to antimonates are, on the whole, similar to the corresponding relations with arsenic. In the higher state of oxidation the acid properties are more pronounced than the basic properties, but antimony, being lower in the same group of the periodic table, is more basic than arsenic.

Reactions in the Wet Way

1. **Hydrogen Sulfide** precipitates from fairly acid solutions the orange-red pentasulfide:

$$2\ Sb^{+++++} + 5\ H_2S \rightarrow 10\ H^+ + Sb_2S_5$$

Antimony pentasulfide is soluble in 12-normal hydrochloric acid, forming antimony *trichloride*, with deposition of sulfur and evolution of hydrogen sulfide:

$$Sb_2S_5 + 6\ HCl \rightarrow 3\ H_2S\uparrow + 2\ S + 2\ SbCl_3$$

It also dissolves (like the trisulfide) in alkali sulfides, and in alkalies and in ammonium hydroxide, but not in ammonium carbonate. By treatment with an alkali sulfide, a thio-salt is obtained,

$$Sb_2S_5 + 3\ S^{--} \rightarrow 2\ SbS_4^{---}$$

which is decomposed by the addition of acids, forming the insoluble pentasulfide with evolution of hydrogen sulfide:

$$2\ SbS_4^{---} + 6\ H^+ \rightarrow 3\ H_2S\uparrow + Sb_2S_5$$

Alkalies dissolve the pentasulfide, forming thio- and oxy-thio salts:

$$Sb_2S_5 + 6\ OH^- \rightarrow SbS_4^{---} + SSbO_3^{---} + 3\ H_2O$$

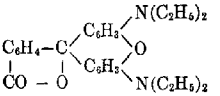
2. **Ammonium Thioacetate** and **Sodium Thiosulfate** behave toward antimony solutions about the same as does hydrogen sulfide.

3. **Hydriodic Acid** reduces antimonic compounds in acid solutions, with separation of iodine (difference from antimonous compounds):

$$Sb^{+++++} + 2\ I^- \rightarrow Sb^{+++} + I_2$$

4. **Rhodamine B, or tetraethylrhodamine,** gives a violet coloration with antimonic acid.

Small quantities of iron do not interfere, but similar tests are obtained with mercury, gold, thallium, bismuth, molybdenum, and tungsten. The dyestuff has the formula



but the composition of the compound produced in the test has not been established. It is necessary for the antimony to be in the quinquevalent state, and this may be accomplished in the hydrochloric acid solution of a sulfide precipitate by adding a little sodium nitrite.

Place on a spot plate 1 ml of the solution obtained by dissolving 10 mg of the dyestuff in 100 ml of water. Add 1 drop of the solution to be tested. If 0.5 γ or more of antimony is present the original light red color of the fluorescent dyestuff will change to violet.

5. **Zinc, Tin, Iron, Aluminum, Magnesium,** and other metals above hydrogen in the potential series reduce antimony compounds to metallic antimony in acid solutions:

$$5\,Zn + 2\,SbO_4^{---} + 16\,H^+ \rightarrow 2\,Sb + 5\,Zn^{++} + 8\,H_2O$$

If an antimony solution is placed in contact with platinum and zinc (both metals touching) the zinc dissolves but the antimony is deposited as a black stain on the platinum.

Zinc, however, unlike tin, iron, or lead, reduces some of the antimony to stibine gas, SbH_3:

$$4\,Zn + SbO_4^{---} + 11\,H^+ \rightarrow 4\,Zn^{++} + 4\,H_2O + SbH_3\uparrow$$

If the stibine is generated in a Marsh apparatus (cf. p. 153), and the gas is conducted through a red-hot glass tube, a mirror of metallic antimony will be deposited, as with arsenic. But since stibine is much more unstable than arsine, and the antimony itself is much less volatile, the mirror is found nearer the heated place than is the case with arsenic — sometimes even before the hottest part of the tube is reached — since the decomposition of the stibine takes place at a much lower temperature than with arsine.

If the stibine is allowed to escape from the tube with the hydrogen, it burns with a pale greenish white flame to water and antimony trioxide. If a piece of glazed porcelain is held directly over the flame, a deposition of metallic antimony is obtained which is unaffected by a solution of sodium hypochlorite (difference from arsenic).

If stibine is allowed to act upon a solution of silver nitrate, a black precipitate of silver antimonide is formed:

$$SbH_3 + 3\,Ag^+ \rightarrow Ag_3Sb + 3\,H^+$$

Solid silver nitrate is turned yellow at first, then black, exactly the same as by arsine (cf. p. 155).

If a mirror is produced in the Marsh test, antimony may be distinguished from arsenic by the fact that the arsenic is easily dissolved by sodium hypochlorite solution. Another method for distinguishing between the two metals is as follows:

Detach the tube containing the mirror from the Marsh apparatus and pass hydrogen sulfide through the tube while heating gently in the reverse direction: arsenic is changed to *yellow* sulfide and antimony to orange sulfide. Pass a stream of dry hydrogen chloride through the tube and the orange sulfide will disappear but the arsenic sulfide will remain.

Reactions in the Dry Way

Antimony compounds impart to the flame a pale, greenish white color. Heated with sodium carbonate on charcoal, a brittle metallic button is obtained, surrounded by a white incrustation.

Compounds containing oxygen are reduced in the upper reducing flame to metal, which is volatile and burns in the upper oxidizing flame to trioxide; the trioxide can be deposited on a glazed porcelain surface. If the deposit is moistened with silver nitrate solution, and ammonia blown upon it, it becomes black, owing to the separation of metallic silver:

$$Sb_2O_3 + 4\ AgNO_3 + 4\ NH_3 + 2\ H_2O \rightarrow 4\ NH_4NO_3 + Sb_2O_5 + 4\ Ag$$

Antimony sulfide fused with potassium cyanide gives metallic antimony and potassium thiocyanate:

$$3\ KCN + Sb_2S_3 \rightarrow 2\ Sb + 3\ KCNS$$

If the reaction takes place in a bulb tube, or in a stream of carbon dioxide, a regulus of metal is obtained and not a mirror as with arsenic.

Heating with sodium carbonate and potassium cyanide in a stream of hydrogen gives rise to an antimony mirror not far from the decomposition zone.

TIN, Sn. At Wt. 118.7, At. No. 50

Density 7.31. M. P. 232°. B. P. 2270° at 755 mm

Occurrence. — Tin does not occur free in nature, but mostly in the form of the dioxide, as tetragonal tinstone, or cassiterite, isomorphous with rutile (TiO_2), zircon, and polianite (MnO_2).

Properties. — Tin is a silver-white metal, which is ductile and malleable at ordinary temperatures, but at low temperatures and near the melting point it is so brittle that it can be powdered. In order to pulverize tin, heat it in a porcelain dish till it melts, remove the flame, and quickly crush the substance with a pestle. It soon cools to about 200°, becomes brittle, and yields a fine powder.

The element owes its name to the Anglo-Saxon word *tin* and its symbol to the Latin word *stannum*. It was known more than 6,000 years ago, and was obtained from Cornwall at an early date. About 180,000 tons of tin are produced annually. When a piece of tin is bent it "cries," owing to friction among the crystals.

Below 20°, gray tin is formed, and objects made of tin often deteriorate in cold weather owing to the formation of this allotropic modification. When once formed it spreads over the metal. Gray tin is often called, therefore, *tin pest*, and at low temperature the gray tin *infects* the sound metal and makes it powdery.

Above 200° orthorhombic tin crystals are formed which are hard and brittle.

Tin forms useful alloys with many metals — silver, brass, bronze, Babbitt metal, type metal, fusible metal, etc.

Tin is soluble in hot, concentrated hydrochloric acid with evolution of hydrogen:

$$Sn + 2\,H^+ \rightarrow Sn^{++} + H_2\uparrow$$

In the presence of platinum the solution takes place more quickly and at a lower temperature. Dilute hydrochloric acid dissolves tin, but very slowly.

Nitric acid, of density 1.2 to 1.3, does not dissolve tin, but oxidizes it to metastannic acid:

$$3\,Sn + 4\,HNO_3 + H_2O \rightarrow 3\,H_2SnO_3 + 4\,NO\uparrow$$

Cold, dilute nitric acid dissolves the metal very slowly, without any evolution of gas, forming ammonium and stannous nitrates.

In this reaction the tin is given two positive charges and a part of the nitrogen of nitric acid is reduced from a positive valence of five (toward oxygen) to a negative valence of three (toward hydrogen), thereby losing eight charges. Thus one molecule of nitric acid oxidizes four atoms of tin, and eight more molecules of nitric acid are required to form stannous nitrate and one to form ammonium nitrate. The whole reaction may be expressed as follows:

$$4\,Sn + 10\,HNO_3 \rightarrow 4\,Sn(NO_3)_2 + NH_4NO_3 + 3\,H_2O$$

Aqua regia dissolves tin, forming stannic chloride:

$$3\,Sn + 4\,HNO_3 + 12\,HCl \rightarrow 4\,NO\uparrow + 8\,H_2O + 3\,SnCl_4$$

Tin dissolves in dilute sulfuric acid very slowly, but readily in hot concentrated acid, forming stannic sulfate, with evolution of sulfur dioxide:

$$Sn + 4\,H_2SO_4 \rightarrow 2\,SO_2\uparrow + 4\,H_2O + Sn(SO_4)_2$$

Tin forms two oxides: stannous oxide, SnO; and stannic oxide, SnO_2. Salts are known corresponding to both these oxides — stannous and stannic salts. The former contain bivalent tin and the latter quadrivalent tin. Tin is more basic in its properties than antimony, but stannous hydroxide is slightly amphoteric (cf. p. 60) and the acid properties of stannic hydroxide are more pronounced.

Stannous Compounds

Stannous oxide (according to the way it is prepared) is either an olive-green or a black powder, which, on being warmed in the air, like all stannous compounds readily changes to stannic oxide. By dissolving stannous oxide (or, better still, the metal itself) in hydrochloric acid, stannous chloride is obtained, which is the most important of all the stannous salts. This salt, with two molecules of water of crystallization, $SnCl_2 \cdot 2\,H_2O$, is the so-called tin salt of commerce.

Fresh crystals of tin salt will dissolve clear in a little water; if more water is added the solution becomes turbid, owing to the formation of a basic salt,

$$SnCl_2 \cdot H_2O \rightleftarrows HCl + Sn(OH)Cl$$

which is readily soluble in hydrochloric acid.

The clear concentrated solution also becomes turbid on standing in the air, owing to the formation of the same basic salt:

$$4\,SnCl_2 + O_2 + 2\,H_2O \rightarrow 4\,Sn(OH)Cl + 2\,Cl_2$$

The chlorine, however, is not set free, but unites with some of the stannous ions, forming stannic ions:

$$Sn^{++} + Cl_2 \rightarrow Sn^{++++} + 2\,Cl^-$$

If tin tetrachloride is treated with metallic tin, the latter goes into solution and the former is reduced to stannous chloride:

$$SnCl_4 + Sn \rightarrow 2\ SnCl_2$$

Consequently, in order to keep a solution of stannous chloride in the stannous condition, hydrochloric acid should be added to prevent the formation of the basic salt, and metallic tin to keep the solution reduced.

Such a solution constantly grows more concentrated, owing to the gradual dissolving of the tin. In order to keep a solution of stannous chloride at a definite concentration (only necessary for purposes of quantitative analysis) the hydrochloric acid solution should be kept out of contact with air in an atmosphere of carbon dioxide without the addition of metallic tin.

Nearly all stannous compounds are colorless; the oxide (as already mentioned) is black and the sulfide dark brown.

Reactions in the Wet Way

1. **Hydrogen Sulfide** produces (in solutions which are not too acid) a brown precipitate of stannous sulfide,

$$Sn^{++} + H_2S \rightarrow 2\ H^+ + \mathbf{SnS}$$

readily soluble in strong hydrochloric acid; therefore no stannous sulfide is precipitated if the solution is very acid. After diluting a strongly acid solution with water, however, stannous sulfide is completely precipitated on saturating the solution with hydrogen sulfide gas.

Stannous sulfide is insoluble in ammonia and ammonium carbonate (difference from arsenic); also in colorless ammonium sulfide (difference from arsenic and antimony); but is readily soluble in yellow ammonium sulfide, forming ammonium thiostannate:

$$\mathbf{SnS} + (NH_4)_2S_2 \rightarrow (NH_4)_2SnS_3$$

If the solution of ammonium thiostannate is treated with any acid, yellow stannic sulfide is precipitated:

$$SnS_3^{--} + 2\ H^+ \rightarrow H_2S\uparrow + \mathbf{SnS_2}$$

2. **Alkali Hydroxides** produce a white precipitate of gelatinous stannous hydroxide,

$$Sn^{++} + 2\ OH^- \rightarrow \mathbf{Sn(OH)_2}$$

which is readily soluble in an excess of the precipitant, forming alkali stannite:

$$\mathbf{Sn(OH)_2} + OH^- \rightarrow H_2O + HSnO_2^-$$

The hydroxide is also readily soluble in hydrochloric acid.

The alkaline solution of an alkali stannite is often changed to brownish black or black (particularly on warming, or when very concentrated caustic alkali is used), owing to the separation of either metallic tin or stannous oxide (cf. p. 125):

From dilute potassium hydroxide solutions there gradually separates on standing, or more rapidly on heating, the black monoxide,

$$HSnO_2^- \rightarrow OH^- + SnO$$

and from quite concentrated alkali the precipitate is almost wholly black metallic tin:

$$2\,HSnO_2^- \rightarrow SnO_3^{--} + H_2O + Sn$$

3. **Ammonia** and **Alkali Carbonates** precipitate the white hydroxide, which is not absolutely insoluble in an excess of the precipitant:

$$Sn^{++} + 2\,NH_4OH \rightarrow Sn(OH)_2 + 2\,NH_4^+$$

$$Sn^{++} + CO_3^{--} + H_2O \rightarrow CO_2\uparrow + Sn(OH)_2$$

A large quantity of tartaric acid, more than is required with antimony, prevents the precipitation.

4. **Ammonium Molybdate** in sulfuric acid solution is reduced and gives a blue color with stannous salts.

The test is more specific and can be used for detecting $SnCl_2$ in the presence of $SbCl_3$ if a precipitate of ammonium phosphomolybdate is used instead of a soluble molybdate. First prepare phosphomolybdic acid by dissolving ammonium phosphomolybdate in aqua regia, evaporating to dryness, and recrystallizing the residue twice from water. Dissolve 5 g in 100 ml of water to make the phosphomolybdic acid solution.

Moisten a strip of filter paper with the reagent, hold it for a short time over vapors of NH_3, and dry. Place a drop of the solution to be tested on the dry paper; a blue color will develop if 0.03 γ of tin is present (Feigl). The test paper can be kept in the dark in a well-stoppered, small flask.

5. **Ammonium Thioacetate** precipitates tin completely as sulfide from hot, dilute acid solutions:

$$C_2H_3OS^- + Sn^{++} + H_2O \rightarrow SnS + HC_2H_3O_2 + H^+$$

6. **Bismuth Nitrate** added in small quantity to an alkaline solution of a tin salt gives a white precipitate of bismuth hydroxide which rapidly changes to black metallic bismuth:

$$2\,Bi^{+++} + 3\,SnO_2^{--} + 6\,OH^- \rightarrow 3\,SnO_3^{--} + 3\,H_2O + 2\,Bi$$

7. **Dimethylglyoxime**, $(CH_3)_2(CNOH)_2$ and **Ferric Chloride** react with stannous ions to form a red coloration due to the formation of the complex ferrous dimethylglyoxime salt.

The reaction between ferrous ions and dimethylglyoxime (p. 210) is very sensitive and has been obtained with 0.04 γ of iron. The stannous ion reduces the ferric ion instantly, and then the ferrous ion reacts with the oxime.

Place 1 drop of the strongly acid stannous solution on a spot plate, add 1 drop of 0.1 *N* ferric chloride solution, and, after one minute, add a small crystal of solid, tartaric acid to prevent the formation of ferric hydroxide. Make the mixture alkaline with ammonia, and if 0.04 γ of tin is present a red coloration will appear.

8. The **Gold Test** is also sensitive. If to a solution of gold chloride a solution containing a trace of stannous chloride is added, finely

divided metallic gold will be precipitated,

$$2\,Au^{+++} + 3\,Sn^{++} \rightarrow 3\,Sn^{++++} + 2\,\mathbf{Au}$$

which appears brown by transmitted light, and bluish green by reflected light.

9. **Hydrogen Peroxide** added to a neutral solution of stannous salt gives a white precipitate of stannic hydroxide on heating.

10. **Mercuric Chloride** produces in solutions of stannous salts a white precipitate of mercurous chloride:

$$2\,HgCl_2 + Sn^{++} \rightarrow Sn^{++++} + 2\,Cl^- + \mathbf{Hg_2Cl_2}$$

But if the stannous chloride is present in excess, the mercurous chloride will be reduced to gray mercury:

$$\mathbf{Hg_2Cl_2} + Sn^{++} \rightarrow Sn^{++++} + 2\,Cl^- + 2\,\mathbf{Hg}$$

11. **Mercuric Chloride and Aniline** react with stannous ions to form finely divided mercury.

The reaction $2\,HgCl_2 + Sn^{++} \rightarrow Sn^{++++} + \mathbf{Hg_2Cl_2} + 2\,Cl^-$ is sensitive but the mercurous chloride formed is white and not easy to see on white filter paper. In alkaline solution, the reaction takes place further and mercury is deposited even when an excess of mercuric salt is present. The solution can be made alkaline by adding alkali hydroxide or ammonia, but aniline is better because its alkalinity is so slight that there is less danger of interference by trivalent antimony.

Dip a piece of paper in strong mercuric chloride solution and dry it. Place 1 drop of the slightly acid solution to be tested on the dry paper, and upon the damp spot place 1 drop of aniline. If 0.6 γ of stannous tin is present, a black or brown spot will form.

If the solution contains tin in the stannic condition, it can be reduced on a watch glass by a small piece of magnesium wire.

12. **Metallic Lead,** as is evident from its position in the electromotive series (cf. pp. 43 and 46), will reduce tin to the metallic state, but the reaction will stop as soon as the concentration of Pb^{++} becomes nearly as large as that of Sn^{++}; when the concentration of Pb^{++} is greater than that of Sn^{++} the reaction will take place in the reverse direction. It requires a relatively low concentration of H^+ to stop these reactions, since both tin and lead are higher in the series than hydrogen. In acid solution, however, metallic lead will reduce Sn^{++++} to Sn^{++} (cf. p. 46).

In acid solutions, **metallic antimony** also reduces stannic salts to the stannous condition:

$$2\,\mathbf{Sb} + 3\,Sn^{++++} \rightarrow 2\,Sb^{+++} + 3\,Sn^{++}$$

13. **Metallic Zinc** precipitates tin from both stannous and stannic solutions as a spongy mass, which adheres to the zinc:

$$Sn^{++} + \mathbf{Zn} \rightarrow Zn^{++} + \mathbf{Sn}$$

The finely divided, spongy metal is easily soluble in strong hydrochloric acid; the experiment must not, therefore, be made in strongly acid solution, or the tin may be loosened from the zinc by the violent evolution of hydrogen and be redissolved by the acid. The test is best made by adding a drop of the (not too acid) solution to a piece of platinum foil, and then placing a piece of bright zinc so that it comes in contact with both the solution and the platinum. The tin is precipitated partly on the zinc and partly on the platinum,* in the form of a gray stain, which disappears from the latter as soon as the zinc is removed, provided the solution is still acid (difference from antimony). If the zinc is kept in contact with the acid until the evolution of hydrogen ceases, the tin stain will not disappear from the platinum, because all the acid has been used up. On the addition of a few drops of concentrated hydrochloric acid to the platinum, the stain quickly disappears with an evolution of hydrogen. The reason why the tin is deposited on the platinum, notwithstanding the presence of acid, is that a galvanic current is formed by the contact of the zinc with the platinum, which flows from the zinc to the platinum; the platinum thus serves as a cathode, and the tin is deposited upon it. On removing the zinc the current stops and the stain disappears.

14. **Oxalic Acid** precipitates white, granular stannous oxalate from neutral or faintly acid solutions of stannous salts:

$$Sn^{++} + H_2C_2O_4 \rightarrow SnC_2O_4 + 2\ H^+$$

Ammonium chloride prevents this reaction. A solution of stannous salt containing ammonium chloride and considerable oxalic acid is not acted upon by hydrogen sulfide.

15. **Potassium Ferricyanide** and **Ferric Chloride** added to an acid solution of a stannous salt give a precipitate of Prussian blue:

$$6\ [Fe(CN)_6]^{---} + 8\ Fe^{+++} + 3\ Sn^{++} \rightarrow 3\ Sn^{++++} + 2\ Fe_4[Fe(CN)_6]_3$$

The reaction is sensitive but is caused by reducing agents other than stannous chloride. The ferricyanide ion is reduced to ferrocyanide ion which gives a blue color with ferric ions.

16. **Sodium Thiosulfate** gradually precipitates the tin from solutions which are not too acid. Sometimes the precipitate is chiefly stannous sulfide:

$$Sn^{++} + S_2O_3^{--} + H_2O \rightarrow SnS + 2\ H^+ + SO_4^{--}$$

Sometimes the precipitate contains stannic sulfide and metastannic acid:

$$6\ Sn^{++} + 2\ S_2O_3^{--} + 9\ H_2O \rightarrow SnS_2 + 5\ H_2SnO_3 + 2\ S + 8\ H^+$$

If the solution is very acid, considerable thiosulfate must be added, because of the reaction:

$$S_2O_3^{--} + 2\ H^+ \rightarrow S + H_2O + SO_2\uparrow$$

and, moreover, the SO_2 has a slight reducing effect with Sn^{++}:

$$3\ Sn^{++} + SO_2 + 6\ H^+ \rightarrow 3\ Sn^{++++} + H_2S\uparrow + 2\ H_2O$$

Stannic Compounds

The stannic compounds (all of which are colorless with the exception of the yellow sulfide, SnS_2) cannot be obtained by dissolving the oxide, SnO_2, from which they are derived, because the oxide is attacked with difficulty by acids. They are obtained indirectly from metallic tin or from stannous compounds.

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* In weakly acid solutions tin is precipitated chiefly on the zinc; in strongly acid solutions, chiefly on the platinum.

The simple stannic compounds are all, more or less readily, hydrolyzed by water, so that the analyst almost never meets with them. The nitrate, $Sn(NO_3)_4$, and the sulfate, $Sn(SO_4)_2$, are quickly decomposed in the cold, into acid and amphoteric stannic hydroxide. The halogen compounds are more stable, and are decomposed only by boiling with considerable water. For the reactions below, therefore, it will be assumed that the tests are made with a solution of stannic chloride.

Stannic chloride is a colorless liquid, which fumes in the air and boils at 120° C. On adding a little water it solidifies, forming crystals of monoclinic hydrates, $SnCl_4 \cdot 3H_2O$, $SnCl_4 \cdot 5H_2O$, $SnCl_4 \cdot 8H_2O$. The salt with 5 H_2O is used commercially as a mordant in dyeing.

On adding more water to these hydrates they dissolve, forming a clear solution, which on boiling (the freshly prepared, dilute solution) gradually becomes turbid, owing to the precipitation of voluminous stannic hydroxide:

$$SnCl_4 + 4\ HOH \rightleftarrows 4\ HCl + Sn(OH)_4$$

If the solution is very dilute it becomes turbid in the cold. The stannic hydroxide thus formed is not precipitated quantitatively, either in the cold or on boiling, because a considerable amount remains in the hydrosol form. By "salting out" the hot solution (best with ammonium nitrate), the stannic hydroxide may be completely precipitated.

A solution of stannic chloride can be most readily obtained for analytical purposes by chlorinating or brominating a solution of stannous chloride.

On adding chlorine to a solution of stannous chloride, stannic chloride is formed in the cold:

$$SnCl_2 + Cl_2 \rightarrow SnCl_4$$

Since, however, chlorine is colorless in a dilute solution, it is difficult to tell when the oxidation is complete: it is more easily ascertained if bromine is used.

On adding strong bromine water, drop by drop with constant stirring, to a solution of stannous chloride, the bromine color will disappear as long as any stannous chloride remains unchanged, and the solution becomes colored by the bromine only when the oxidation is complete. The solution then contains a mixture of stannic chloride and stannic bromide:

$$2\ SnCl_2 + 2\ Br_2 \rightarrow SnCl_4 + SnBr_4$$

Just as platinum tetrachloride combines with hydrochloric acid to form chloroplatinic acid, so tin tetrachloride unites with hydrochloric acid, forming chlorostannic acid, H_2SnCl_6, and yields, like the former, beautifully crystalline, easily soluble salts with the alkalies, of which the ammonium salt $(NH_4)_2[SnCl_6]$ is an article of commerce, being known as "pink salt." The above-mentioned stannic chloride, $SnCl_4$, is sometimes designated as α-stannic chloride, to distinguish it from a compound (to be described later) known as β-stannic chloride (stannyl chloride).

Treatment of Tin Dioxide

Tin dioxide as it occurs in nature, and the artificially produced oxide after strong ignition, are both insoluble in all acids. They can be brought into solution by the following methods:

1. Fusion with sodium carbonate and sulfur,
2. Fusion with caustic potash or soda,
3. Fusion with potassium cyanide,
4. Reduction by hydrogen at a high temperature.

(1) *Fusion with Sodium Carbonate and Sulfur.* — Place the dry substance in a small porcelain crucible, mix with six times as much anhydrous sodium carbonate and sulfur (equal parts mixed together), cover the crucible, and heat over a small flame until the excess of sulfur has distilled off and burned. This operation requires about twenty minutes. Allow the crucible to cool and then treat its contents with hot water, and filter if necessary:

$$2\,SnO_2 + 2\,Na_2CO_3 + 9\,S \rightarrow 3\,SO_2 + 2\,Na_2SnS_3 + 2\,CO_2$$

If iron, lead, copper, or any other metal that forms a sulfide insoluble in water and ammonium polysulfide is present, it remains undissolved as sulfide, and is separated from the tin by filtration.

(2) *Fusion with Sodium Hydroxide.* — Melt the sodium hydroxide in a silver crucible, placed within a porcelain crucible to protect the silver from the injurious action of the gas flame. When the fusion has become quiet, owing to the expulsion of all the excess water, cool somewhat and add the finely powdered dry tin dioxide. Heat until the fusion mixture is clear. After cooling dissolve the melt in water:

$$SnO_2 + 2\,NaOH \rightarrow Na_2SnO_3 + H_2O$$

Stannic oxide is not completely attacked by fusion with sodium or potassium carbonate.

(3) *Fusion with Potassium Cyanide.* — Melt some potassium cyanide in a porcelain crucible, add the powdered stannic oxide, and fuse the mixture until the separated tin has melted together:

$$SnO_2 + 2\,KCN \rightarrow 2\,KCNO + Sn$$

After cooling, extract the mass with water, filter off the tin, flatten it into foil, and dissolve it in concentrated hydrochloric acid.

(4) *Reduction in a Stream of Hydrogen.* — Place the substance in a porcelain boat and insert the boat in a glass tube, open at both ends, which is made of difficultly fusible glass. Pass hydrogen through the tube in the cold until the air has been driven out, and then heat to dull redness until no more water is formed:

$$SnO_2 + 2\,H_2 \rightarrow 2\,H_2O + Sn$$

Finally cool and dissolve the metal in hydrochloric acid.

α-Stannic Compounds

Reactions in the Wet Way

1. **Hydrochloric** and **Sulfuric Acids** produce in moderately concentrated solutions of stannic chloride no precipitation, even on long standing (difference from β-stannic compounds). In very dilute sulfuric acid solutions a precipitate of basic sulfate is sometimes obtained. In very dilute hydrochloric acid solutions, also, a slight turbidity is often formed, which increases on boiling the solution:

$$SnCl_4 + 4\,HOH \rightleftarrows 4\,HCl + Sn(OH)_4$$

2. **Alkali Hydroxides.** — On adding caustic alkali to a solution of a stannic salt, a voluminous, gelatinous, white precipitate is obtained:

$$SnCl_4 + 4\,OH^- \rightarrow 4\,Cl^- + Sn(OH)_4$$

The precipitate has the above formula when dried in the air, and the formula H_2SnO_3 if dried over sulfuric acid.

The precipitate dissolves readily in an excess of alkali hydroxide, forming salts which are not derived from either of the above compounds, but from $H_2[Sn(OH)_6]$, which has itself never been isolated:

$$Sn(OH)_4 + 2\,KOH \rightarrow K_2[Sn(OH)_6]$$

The hydroxide dissolves in ammonia also, but only in the absence of ammonium salts. By dissolving in alkali hydroxide, stannic hydroxide behaves as an acid, and according to Bellucci and Parravano,* the hexahydroxystannic acid stands in the same relation to chlorostannic acid as hexahydroxyplatinic acid to chloroplatinic acid:

$H_2[PtCl_6]$	$H_2[SnCl_6]$
$H_2[Pt(OH)_6]$	$H_2[Sn(OH)_6]$

The salts of hexahydroxystannic acid are designated briefly as stannates, or α-stannates, to distinguish them from the β-stannates or metastannates, which are derived from the polymer $(H_2SnO_3)_5$ (see p. 175).

The ready solubility of α-stannic acid in cold dilute mineral acids is very characteristic. It dissolves promptly in hydrochloric, nitric, and sulfuric acids, behaving in this respect, as a base. By boiling the dilute acid solution (particularly the sulfuric acid solution) stannic acid is reprecipitated, which is soluble in cold dilute acids provided the boiling has not been continued too long. In the latter case the β-stannic acid is formed, which is insoluble in dilute acids.

3. **Alkali Sulfates** produce no precipitation in the cold (difference from stannyl chloride), but on boiling all the tin is precipitated as hydroxide.

4. **Ammonia** precipitates stannic acid from a solution of stannic chloride; tartaric acid prevents the precipitation (difference from β-stannic acid).

5. **Potassium Carbonate** precipitates stannic acid from stannic chloride solutions; the precipitate dissolves completely in an excess of the reagent (difference from β-stannic acid):

$$SnCl_4 + 2\,K_2CO_3 + 2\,H_2O \rightarrow 4\,KCl + 2\,CO_2\uparrow + Sn(OH)_4$$

$$Sn(OH)_4 + K_2CO_3 \rightarrow K_2SnO_3 + 2\,H_2O + CO_2\uparrow$$

6. **Sodium Carbonate** behaves similarly, but the precipitate is not so easily dissolved by an excess.

β-Stannic Compounds
(*Metastannates*)

Reactions in the Wet Way

By the oxidation of metallic tin with hot nitric acid of density 1.3 stannic nitrate is first formed, which, by boiling with water, is completely hydrolyzed, forming nitric acid and metastannic acid.

* *Z. anorg. Chem.*, **45**, p. 156 (1905).

Metastannic acid is a white powder insoluble in nitric acid, and when dried over sulfuric acid has the formula H_2SnO_3. This is of the same empirical composition as the hydroxide precipitated by treating a stannic chloride solution with alkali hydroxide, though differing essentially from it in many reactions.

Although the α-stannic acid (as already mentioned) is easily soluble in dilute mineral acids, the β-stannic acid is practically insoluble therein.

1. If the β-stannic acid is treated for a short time with concentrated hydrochloric acid, a chloride is formed which is insoluble in hydrochloric acid, but readily soluble in water. The solution contains the so-called β-stannic chloride (though the designation stannyl chloride would be more suitable) of the composition $Sn_5O_5Cl_2(OH)_8$.*

2. On treating the aqueous solution of stannyl chloride with hydrochloric acid, almost all the tin is reprecipitated in the form of a highly chlorinated compound of the composition $Sn_5O_5Cl_4(OH)_6 \cdot 4\,H_2O$.†

3. If an aqueous solution of stannyl chloride is heated to boiling, almost all the tin is precipitated as β-stannic acid, which is insoluble in dilute acids.

This differing behavior of the two acids, as well as of the two chlorides, can be explained as follows: Silicic acid, which is closely related to stannic acid, exists in innumerable silicates in different polymeric forms. Thus, with the minerals of the pyroxene and amphibole groups, wollastonite, $CaSiO_3$, is a derivative of ordinary metasilicic acid, and tremolite, $CaMg_3Si_4O_{12}$, is a derivative of $(H_2SiO_3)_4$.‡ It is highly probable that the stannic acid can exist in analogous polymers. One of these polymers apparently corresponds to the composition $(H_2SnO_3)_5$.

If such a compound is treated with hydrochloric acid, the hydroxyl groups will, first, be replaced by chlorine, and a compound will be obtained containing tin, oxygen, and chlorine, *e.g.*, $Sn_5O_5Cl_{10}$. This hypothetical compound of the β-stannic acid is hydrolyzed, forming different chlorides of varying solubilities. Thus R. Engel found that the chloride $Sn_5O_5Cl_2(OH)_8$ is soluble in water; and Weber showed that, from an aqueous solution of the latter, hydrochloric acid precipitates the compound $Sn_5O_5Cl_4(OH)_6 \cdot 4\,H_2O$.

The reaction which takes place on dissolving the β-stannic acid in hydrochloric acid and water may be expressed satisfactorily by the following equations:

$$\underset{\substack{\beta\text{-stannic acid}\\ \text{or}\\ \text{Metastannic acid}}}{Sn_5O_5(OH)_{10}} + 10\,HCl \rightleftarrows 10\,H_2O + Sn_5O_5Cl_{10}\ (\text{insoluble in HCl})$$

$$Sn_5O_5Cl_{10} + 8\,H_2O \rightleftarrows 8\,HCl + Sn_5O_5Cl_2(OH)_8\ (\text{soluble in water})$$

$$Sn_5O_5Cl_2(OH)_8 + 2\,HCl \rightleftarrows 2\,H_2O + Sn_5O_5Cl_4(OH)_6\ (\text{insoluble in HCl})$$

On boiling the aqueous solution, complete hydrolysis takes place:

$$Sn_5O_5Cl_2(OH)_8 + 2\,HOH \rightarrow 2\,HCl + Sn_5O_5(OH)_{10}$$

If the β-stannic acid is treated for a long time with concentrated hydrochloric acid, the Sn_5O_5 group is finally broken down, and the tin goes into solution in the form of ordinary α-stannic chloride:

$$Sn_5O_5(OH)_{10} + 20\,HCl \rightarrow 15\,H_2O + 5\,SnCl_4$$

Other reactions of stannyl chloride (β-stannic chloride) are:

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* R. Engel, *Chem. Ztg.*, **1897**, pp. 309 and 859.

† Weber, *Jahresber.*, **1869**, 244 and *Pogg. Ann.*, **122**, 358.

‡ Goth, *Tabellarische Uebersicht d. Min.*, **1898**, p. 148.

4. **Alkali Hydroxide** throws down in solutions of stannyl chloride a voluminous precipitate of β-stannic acid, which does not dissolve in an excess of the concentrated precipitant, but forms a β-stannate easily soluble in dilute caustic potash solution:

$$Sn_5O_5Cl_2(OH)_8 + 2\,KOH \rightarrow 2\,KCl + \underset{\beta\text{-Stannic acid}}{Sn_5O_5(OH)_{10}}$$

$$Sn_5O_5(OH)_{10} + 2\,KOH \rightarrow 2\,H_2O + \underset{\text{Potassium } \beta\text{-stannate}}{Sn_5O_5(OK)_2(OH)_8}$$

By long treatment of the potassium β-stannate with concentrated caustic potash, it gradually goes into solution, forming potassium α-stannate. This change takes place more readily by fusing β-stannic acid with solid potassium hydroxide in a silver crucible.

If a dilute solution of a mineral acid is added to the β-potassium stannate, a voluminous precipitate is formed, consisting partly of β-stannic acid (insoluble in an excess of mineral acids) and partly of α-stannic acid (readily soluble in an excess of the acid). The latter compound is formed when a very concentrated solution of caustic potash was used in forming the potassium salt.

5. **Alkali Sulfates** cause the same reaction as sulfuric acid.

6. **Ammonia** also precipitates β-stannic acid, even in the presence of tartaric acid (difference from α-stannic chloride).

As we have seen, the α-compounds may be readily changed into β-compounds, and conversely. *The dilute aqueous solutions of the α-compounds are gradually changed, at the ordinary temperature, into β-compounds, but more quickly on boiling;* thus stannic chloride changes to stannyl chloride:

$$5\,SnCl_4 + 13\,H_2O \rightarrow 18\,HCl + Sn_5O_5Cl_2(OH)_8$$

The β-compounds are changed into α-compounds by boiling with concentrated hydrochloric acid or with concentrated caustic potash.

7. **Ammonium Thioacetate** precipitates stannic sulfide from hot, acid solutions:

$$2\,C_2H_3OS^- + Sn^{++++} + 2\,H_2O \rightarrow SnS_2 + 2\,HC_2H_3O_2 + 2\,H^+$$

8. **Hydrogen Sulfide** precipitates (from not too acid solutions) yellow stannic sulfide from both the α- and the β-compounds:

$$SnCl_4 + 2\,H_2S \rightleftarrows 4\,HCl + SnS_2$$

$$Sn_5O_5Cl_2(OH)_8 + 10\,H_2S \rightleftarrows 2\,HCl + 13\,H_2O + 5\,SnS_2$$

From β-stannic solutions hydrogen sulfide produces a precipitate, but very slowly, the SnS_2 remaining largely in the hydrosol form. By the addition of salts it is coagulated, separating out in a flocculent form, usually mixed with β-stannic acid. If the stannyl chloride solution is heated on the water-bath in a pressure flask, the tin is quickly precipitated as greenish yellow sulfide. Although stannic sulfide is yellow when pure, it often appears brown when precipitated with other metallic sulfides by hydrogen sulfide.

Stannic sulfide is soluble in hydrochloric acid; hydrogen sulfide will cause no precipitation, therefore, if the solution is very acid. If such a solution, saturated with hydrogen sulfide, is greatly diluted, the sulfide will precipitate out.

The yellow sulfide is the thio-anhydride of the thio-acid; it dissolves, therefore, in alkali sulfide, forming salts soluble in water:

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2SnS_3$$

Acids precipitate from such a solution the yellow stannic sulfide

$$SnS_3^{--} + 2\,H^+ \rightarrow H_2S\uparrow + SnS_2$$

The sulfide is slightly soluble in ammonia but scarcely at all in ammonium carbonate (difference from arsenic). By means of concentrated nitric acid it is easily oxidized to β-stannic acid; or by roasting in the air it can be completely changed to tin dioxide.

The sulfide obtained in the dry way, known as "mosaic gold," is not attacked by nitric acid, and is also insoluble in alkali sulfides. It dissolves on treatment with aqua regia, forming stannic chloride with separation of sulfur. Like native tinstone, it is most readily brought into solution by fusing with sodium carbonate and sulfur (see p. 172).

Tin has a distinct tendency to form complex ions from which hydrogen sulfide does not give the sulfide precipitate. Thus oxalic acid prevents the precipitation of tin (35 to 40 parts of oxalic acid to 1 of tin). Similarly, hydrofluoric acid and phosphoric acid prevent the formation of stannic sulfide.

9. **Mercuric Chloride** produces no precipitation in solutions of stannic salt.

10. **Metallic Iron** reduces stannic chloride to stannous chloride but not to the metallic condition:

$$Sn^{++++} + Fe \rightarrow Fe^{++} + Sn^{++}$$

This reaction takes place even in the cold. It also takes place on boiling with copper or with antimony:

$$2\,Cu + Sn^{++++} \rightarrow Sn^{++} + Cu_2^{++}$$

$$2\,Sb + 3\,Sn^{++++} \rightarrow 3\,Sn^{++} + 2\,Sb^{+++}$$

11. **Metallic Zinc** precipitates spongy, metallic tin:

$$2\,Zn + Sn^{++++} \rightarrow Sn + 2\,Zn^{++}$$

If the zinc is in contact with platinum, the tin does not deposit upon the platinum, as does antimony, but upon the zinc.

12. **Sodium Thiosulfate** precipitates a mixture of stannic hydroxide, stannic sulfide, and sulfur when added to an acid solution of stannic salt:

$$Sn^{++++} + 2\,S_2O_3^{--} + 2\,H_2O \rightarrow SnS_2 + 4\,H^+ + 2\,SO_4^{--}$$

$$Sn^{++++} + 2\,S_2O_3^{--} + H_2O \rightarrow H_2SnO_3 + 2\,S + 2\,SO_2\uparrow$$

13. **Sulfuric Acid** precipitates from solutions of stannyl chloride white stannyl sulfate, which on being washed with water is completely changed to β-stannic acid (difference from α-stannic chloride).

Reactions in the Dry Way

If a tin salt is heated with soda (or potassium cyanide) on charcoal, usually only a small malleable button is obtained, which, on taking away the flame, is immediately covered with a white coating of oxide. This can be observed when the flame is allowed to play upon the fusion. If the product is crushed in an agate mortar, a small flake of metallic tin is obtained, which can be distinguished from silver and lead by its insolubility in nitric acid, and by its solubility in hydrochloric acid. This reaction is particularly suitable for the charcoal-stick test. The borax bead which has been colored pale blue by copper becomes a transparent ruby-red in the reducing flame if a trace of tin is added. This is a very sensitive reaction.

By heating stannous or stannic sulfide in chlorine, or by igniting it with a mixture of 5 parts ammonium chloride and 1 part ammonium nitrate, complete volatilization of the tin as stannic chloride takes place. By using a stream of carbon dioxide which has passed through bromine, stannic bromide is formed and distils off.

All tin compounds are reduced to metallic tin by heating with potassium cyanide.

Hydrogen formed from zinc and hydrochloric acid in the presence of a soluble or insoluble tin salt imparts to the non-luminous flame of the Bunsen burner a characteristic blue color. The cause of this effect is unknown, but it is not due to the formation of zinc hydride as has been assumed. To carry out the test, which can be obtained with 0.03 γ of tin, place the substance or solution to be tested in a porcelain dish and add considerable concentrated hydrochloric acid and a few pieces of stick zinc. Stir the mixture with a test tube containing cold water and hold the test tube in the non-luminous flame of the Bunsen burner. If tin is present, a blue flame mantle will form around the test tube.

ANALYSIS OF GROUP II

Gold and platinum are two well-known metals which really belong to this group, but they are seldom present in large quantities in ordinary mineral analysis and the detection of small quantities is so important that it is customary to test for them separately as will be explained in Part V.

The metals of the second group are precipitated as sulfides by means of hydrogen sulfide in the presence of 0.3-normal mineral acid. The theory governing the precipitation of sulfides is discussed on pp. 25, 51, 210, 248. In 0.3-normal mineral acid, the concentration of sulfide ions, formed by the ionization of hydrogen sulfide, is made so small that the solubility products of the sulfides of zinc, nickel, cobalt, iron, and manganese are not reached unless large quantities of these elements are present in solution. In quantities up to 0.5 g of metal, zinc sulfide is the only one which is at all likely to precipitate in acid of this concentration, and then only when it is carried down with a considerable quantity of some second-group metal. The solubility product of lead sulfide is about 4.2×10^{-28}, and that of cadmium sulfide is 3.6×10^{-29}, while that of zinc sulfide is 1.2×10^{-23}. Compared with mercuric sulfide, with its solubility product of 4.0×10^{-53}, lead sulfide is quite soluble, but compared with zinc sulfide, it is much less soluble. In precipitating these sulfides there is some tendency for the sulfide precipitate to carry down with it some of the metals of the succeeding groups partly by adsorption, but this tendency is so slight that even with zinc the test is usually obtained in the proper place when as much as 2 mg are originally present.

The solubilities of the sulfides of the second group vary so greatly that it is possible to separate them from one another by regulating the acid concentration so that enough sulfide ions are furnished by hydrogen sulfide to precipitate one metal and not another. For the same reason, when hydrogen sulfide is passed into the acid solution, the most insoluble sulfide is precipitated first and very little, if any, of a more soluble sulfide is formed until the precipitation of the former is complete. In this respect the behavior of arsenic forms an apparent exception; but this is due, as already pointed out (p. 148), to the absence of an appreciable quantity of arsenic cations in the solution of an arsenate. The order in which the metals are precipitated as sulfides from cold solutions, as the acid concentration is progressively decreased, is approximately as follows: arsenic, mercury, and copper; antimony, bismuth, and stannic tin; cadmium, lead, and stannous tin; zinc, iron, nickel, co-

balt, and manganese. It will be noticed that zinc is placed a little in front of nickel and cobalt in this arrangement. This is the proper order for the precipitation, but after the sulfides have been formed a short time, nickel and cobalt sulfides become less soluble than freshly precipitated cadmium, lead, or stannous sulfide.

The theory of the dissolving of the sulfides is indicated on pages 210 and 240. The more soluble sulfides can be dissolved by merely increasing the concentration of the hydrogen ion. Thus the sulfides of antimony, tin, lead, cadmium, etc., can be dissolved by treatment with concentrated hydrochloric acid. Heating the solution to expel hydrogen sulfide hastens the dissolving, but the most effective expedient is to add an oxidizing agent, which oxidizes the sulfide ions as fast as they are formed in solution. Thus even mercuric and arsenic sulfides will dissolve readily on being treated with aqua regia or with bromine water.

The method to be described for analyzing this group of cations is that worked out by A. A. Noyes and his students. The original precipitate of sulfides is treated with sodium polysulfide solution which dissolves the sulfides of *mercury, arsenic, antimony,* and *tin,* leaving behind the sulfides of *lead, bismuth, copper,* and *cadmium* which do not dissolve, except in small quantities, either in sodium polysulfide or in ammonium polysulfide.

Most of the sulfides of the copper group show a slight tendency to dissolve in either sodium or ammonium polysulfide. Thus 5 to 10 mg of CuS and 0.5 to 1.0 mg of HgS may dissolve in ammonium polysulfide. None of the sulfides, however, dissolve to any extent in ammonium monosulfide. In sodium polysulfide, of the concentration recommended, not more than 1 mg of copper and bismuth sulfides dissolve under normal conditions; the other sulfides of the copper group are even less soluble in sodium polysulfide. The advantage of using sodium polysulfide lies in the fact that it accomplishes in most cases a cleaner separation of the tin group from the copper group than does ammonium polysulfide. In the absence of copper, it is sometimes better to use ammonium sulfide, rather than sodium sulfide, for separating the thio-acids from the thio-bases. When this reagent is used, the HgS is undissolved, and goes into the copper group and is undissolved by the HNO_3 in Table III, § 1. The HgS is dissolved and tested with $SnCl_2$ as described in Table IV, § 3.

TABLE II. — SEPARATION OF THE COPPER AND TIN GROUPS

Solution may contain cations of all the metals except silver and mercurous mercury. *Make the solution 0.3-normal in HCl and saturate with H_2S. Filter and examine the filtrate for Groups III, IV and V. Treat the precipitate with Na_2S_1 solution.* (1)

Residue: PbS, Bi_2S_3, CuS, CdS. *Examine by Table III.* (2)	Solution: $[HgS_2]^{--}$, $[AsS_4]^{---}$, $[SbS_4]^{---}$, $[SnS_3]^{--}$. *Add HCl.* (3)	
	Precipitate: HgS, As_2S_5 Sb_2S_5, SnS_2, S. (4)	Filtrate: NaCl. *Reject.*

PROCEDURE

1. The filtrate from Group I should have a volume of about 100 ml and should contain about 30 milliequivalents of HCl or HNO_3 (*i.e.*,

5 ml of 6 *N* solution) or 50 milliequivalents of H_2SO_4. Pour this solution, without paying any attention to any precipitate of BiOCl or SbOCl that may appear on diluting the filtrate from Group I, into a 200-ml Erlenmeyer flask which is provided with a two-holed rubber stopper carrying a right-angled tube that reaches nearly to the bottom of the flask. Introduce a slow current (about 3 bubbles per second) of H_2S until, upon closing the second hole in the stopper and shaking the flask, the gas will no longer bubble into the solution. Filter, wash the precipitated sulfides with hot water, heat the filtrate to boiling, and introduce H_2S into the hot solution for 10 minutes longer.

If a yellow precipitate of As_2S_3 forms by this second treatment, filter it off,* add 5 ml of 12 *N* HCl and evaporate just to dryness. Add to the residue 10 ml of 6 *N* HCl, saturate with H_2S while cold, then heat to about 80° and introduce H_2S for 10 minutes longer. Filter off the precipitated sulfide, wash it with hot water, and unite it with that originally obtained. Examine the filtrate for cations of Groups III, IV, and V. (Tables V–VIII inclusive.)

2. Transfer the precipitated sulfides to a porcelain dish and add 3 to 10 ml of sodium polysulfide solution. Cover the dish and heat gently for a short time with constant agitation. Dilute with 10 ml of water, filter, and wash with hot water. Examine the residue by the method outlined in Table III and the solution according to § 3.

3. Add hydrochloric acid to the sodium sulfide extract until the stirred solution is acid to litmus, then add 1 ml more of 6-normal acid. Shake well and filter. (If the precipitate is all sulfur, as can be determined by comparing the color with that produced by adding 5 ml of 6-normal acid to 3 ml of sodium sulfide reagent diluted with 7 ml of water, it is unnecessary to test for mercury, arsenic, antimony, or tin. In case of doubt, transfer the precipitate to a casserole and heat a short time with 8 ml of 6-normal NH_4OH; this dissolves arsenic sulfide readily and also small quantities of antimony and tin sulfide. Filter, noting that if mercury is present the residue will consist of *black* HgS and sulfur, together possibly with small quantities of brownish black Bi_2S_3 and CuS. Unless the dark color is apparent there is no need of testing further for mercury. To the ammoniacal filtrate, add 5 drops of $(NH_4)_2S$ reagent, heat to boiling, and filter if necessary. Add 10 ml of water, acidify with hydrochloric acid, and shake well; the presence of arsenic, antimony, and tin will be shown by the color of any pre-

* If a precipitate of As_2S_3 is left in the solution it will eventually dissolve during the evaporation, by the HCl and HNO_3, with formation of H_3AsO_4 and H_2SO_4. This will cause precipitation of Ba^{++} as $BaSO_4$ which may be mistaken for sulfur.

cipitated sulfide, but it is necessary to remember that a mixture of antimony and tin sulfides gives a brown color in many cases.) Reject the filtrate and examine the precipitate, produced by adding hydrochloric acid to the sodium sulfide solution, by the method outlined in Table IV.

TABLE III.—ANALYSIS OF THE COPPER GROUP

<table>
<tr><td colspan="5">Residue from Table II: PbS, Bi_2S_3, CuS, CdS. Boil with 3-normal HNO_3 and filter. (1)</td></tr>
<tr><td rowspan="4">Residue: S usually contaminated with negligible quantities of sulfides. Reject.</td><td colspan="4">Solution: Pb++, Bi+++, Cu++ Cd++. Add H_2SO_4, evaporate, dilute and filter. (2)</td></tr>
<tr><td rowspan="3">Precipitate: $PbSO_4$. Dissolve in NH_4OAc and add K_2CrO_4. A yellow precipitate of $PbCrO_4$ shows the presence of lead. (3)</td><td colspan="3">Filtrate: Bi+++, Cu++, Cd++. Add NH_4OH in excess and filter. (4)</td></tr>
<tr><td>Precipitate: $Bi(OH)_3$. Add Na_2SnO_2. Black residue is Bi. (5)</td><td colspan="2">Filtrate: $[Cu(NH_3)_4]^{++}$, $[Cd(NH_3)_4]^{++}$.</td></tr>
<tr><td>A blue solution shows Cu. If in doubt, add $HC_2H_3O_2$ and $K_4[Fe(CN)_6]$ to a small portion. Red precipitate is $Cu_2[Fe(CN)_6]$. (6)</td><td>To the larger part of the solution add H_2SO_4 and Fe. Filter and saturate the filtrate with H_2S. Yellow precipitate shows Cd. (7)</td></tr>
</table>

PROCEDURE

1. Transfer the residue from the Na_2S_2 treatment to a casserole, add 5–15 ml of 3 *N* HNO_3, stir and heat slowly to boiling. After boiling 3 minutes, filter and reject the residue. (In some cases it may contain nearly 2 mg of Hg. It can be tested as described in (§3) of the Procedure under Table IV.) Examine the solution by (2).

2. To the HNO_3 solution obtained in (1) add 3 ml of 18 *N* H_2SO_4 and evaporate in a casserole until dense white fumes of H_2SO_4 are evolved. If a large residue separates, add 2 ml more of the 18 *N* H_2SO_4. Cool the mixture and pour it cautiously, a little at a time, into 10 ml of cold water in a test tube, cooling the tube after each addition. After 5 minutes' standing, filter and wash the precipitate with 2 *N* H_2SO_4 and then with 5 ml of cold water. Examine the filtrate by (4) and the precipitate by (3).

Sometimes, when considerable bismuth is present, a part of the Bi is precipitated as basic sulfate on adding the water. This precipitate is not so finely crystalline as $PbSO_4$. If the precipitate appears to contain the basic Bi salt, treat it with 10 ml of hot 6 *N* HCl, add 3 ml of 18 *N* H_2SO_4, and repeat the evaporation. Then on diluting no precipitate of basic bismuth sulfate should be formed, as the greater part of the Bi will go into the previous filtrate from the sulfuric acid treatment.

3. Dissolve the $PbSO_4$ precipitate formed in (2) by pouring small portions of hot 3 *N* ammonium acetate solution through the filter. Do not use more than 25 ml in all, and wash the filter with hot water after the addition of each portion of acetate. To the solution thus obtained add a few drops of K_2CrO_4 solution and 5 ml of 6 *N* acetic acid. *A yellow precipitate of $PbCrO_4$ shows the presence of lead.*

4. Neutralize the filtrate from the $PbSO_4$ precipitation (2) with NH_4OH, adding enough to impart a strong odor of NH_3 to the solution. *A blue solution shows the presence of copper. A white precipitate indicates the presence of bismuth.* Filter and wash the precipitate thoroughly with hot, dilute ammonium hydroxide. Examine the precipitate by (5) and the filtrate by (6) and (7).

5. Pour through the filter containing the well-washed precipitate of $Bi(OH)_3$ a cold, freshly prepared solution of Na_2SnO_2. (Take a few drops of $SnCl_2$ solution, add 5 ml of water and NaOH solution in small portions until the precipitate of $Sn(OH)_2$ dissolves.) *An immediate blackening of the precipitate shows Bi to be present.* (Cf. p. 125.)

6. Take one-fourth of the filtrate from the $Bi(OH)_3$ precipitation (4) for the copper test and the remainder for the cadmium test. For the copper test, make the ammoniacal solution acid with acetic acid and add a drop of $K_4Fe(CN)_6$ solution. *A red precipitate of $Cu_2[Fe(CN)_6]$ forms if copper is present.*

7. To test for cadmium, add 6 *N* H_2SO_4 to the ammoniacal solution until 5 ml in excess of the amount necessary to neutralize the solution have been used. Heat to about 50°, add about 0.5 g of iron powder if copper was found present, and shake the mixture gently for about one minute. Filter, add a few drops of 6 *N* H_2SO_4 if the filtrate is turbid, and saturate at once with H_2S. *A yellow precipitate of CdS shows cadmium to be present.* If a black precipitate is obtained, due to the incomplete removal of the copper by the iron or to the presence of Hg if iron was not used, heat the precipitate with 5 ml of 3 *N* HNO_3, evaporate with 2 ml of 18 *N* H_2SO_4, dilute with 15 ml of water, treat with iron powder again, filter, and saturate with H_2S. By this treatment any Cu, Pb, or Hg is removed. If arsenic or antimony is present in the sample being analyzed it is always well to test this yellow precipi-

tate with 10 ml of hot NH_4OH containing a little $(NH_4)_2S$ to dissolve sulfides of arsenic, antimony, and tin. Instead of proceeding as just described, the following procedure is excellent:

7a. If the ammoniacal solution is blue, add potassium cyanide solution until it is colorless, or only a few drops if the solution is already colorless. Pass hydrogen sulfide into the solution for half a minute. *A yellow precipitate of cadmium sulfide is formed if cadmium is present.* A red precipitate of $(CSNH_2)_2$ may be formed if too much H_2S is added (p. 135).

NOTE

Sometimes a small black precipitate is obtained in the cadmium test; it is most likely due to a little mercury or lead that was not properly removed from the solution. In such cases, filter off the precipitate, wash it with water until free from cyanide, and boil gently for five to ten minutes in a covered dish with about 15 ml of 1.2-normal sulfuric acid (6-normal acid diluted with four volumes of water). This serves to dissolve cadmium sulfide, but will not dissolve copper or mercury sulfides and should convert lead sulfide into lead sulfate. Filter, dilute with three times as much water, and saturate with hydrogen sulfide. A yellow precipitate of cadmium sulfide will now be obtained if cadmium is present.

TABLE IV. — ANALYSIS OF THE ARSENIC-TIN GROUP

Precipitate from Table II: HgS, As_2S_5, Sb_2S_5, SnS_2, S. *Heat with 12-normal HCl.* (1)

Residue: HgS, As_2S_5, S. *Add NH_4OH.* (2)		Solution: $HSbCl_4$, H_2SnCl_6. Dilute, heat and saturate with H_2S. (5)	
Residue: HgS, S. *Add HCl and $KClO_3$. Test for mercury with $SnCl_2$.* A precipitate of white Hg_2Cl_2 or of gray Hg_2Cl_2 + Hg shows the presence of mercury. (3)	Solution: AsS_4^{---}, $AsSO_3^{---}$. *Evaporate almost to dryness, add HNO_3, evaporate again and add NH_4OH. Filter if necessary, and add $Mg(NO_3)_2$.* A white precipitate should be $MgNH_4AsO_4$. *Filter, wash the precipitate with a little water and add $AgNO_3$ and $HC_2H_3O_2$.* Red residue of Ag_3AsO_4 shows As is present. (4)	Precipitate: Sb_2S_3. *Dissolve in HCl and add metallic tin.* A black deposit insoluble in NaBrO shows the presence of Sb. (6)	Solution: H_2SnCl_6. *Partly neutralize and test with H_2S. Evaporate without filtering and boil with metallic antimony. Test for stannous tin with $HgCl_2$.* A white or gray precipitate shows Sn is present. (7).

PROCEDURE

1. Transfer the sulfide precipitate (drained as dry as possible by suction) to a test tube and heat it in boiling water for ten minutes with 10 ml of 12-normal hydrochloric acid. Then introduce hydrogen sul-

fide into the hot solution for one minute to precipitate traces of mercury and arsenic, slowly add 3 ml of water while stirring, and filter through a dry filter, using suction. The filter should be placed upon a smaller hardened filter and should be fitted closely to the funnel. Wash the residue first with 6-normal HCl and then with hot water. Examine the filtrate of $HSbCl_4$ and H_2SnCl_6 by § 5 and the residue for arsenic and mercury by § 2.

2. Warm and stir the residue with about 10 ml of 6-normal ammonium hydroxide which dissolves the arsenic and does not affect the mercuric sulfide. Filter and wash this residue with dilute ammonium hydroxide. Examine the filtrate for arsenic by § 4.

3. Digest the residue of mercuric sulfide and excess of sulfur with 5 ml of hydrochloric acid and a little potassium chlorate. Boil until the odor of chlorine disappears, dilute to 15 ml, and add powdered potassium chlorate, a little at a time, until the black residue of HgS disappears. Boil the solution until it no longer smells of chlorine, but do not evaporate, because $HgCl_2$ is volatile. Replace the acid that evaporates, dilute the chlorine-free liquid with 10 ml of water, and filter. To the filtrate add a few drops of $SnCl_2$ solution, then 2–5 ml more. *A white precipitate of Hg_2Cl_2, or a darker one containing some free Hg, indicates the presence of mercury.*

4. Evaporate the ammoniacal solution of ammonium thioarsenate and arsenate nearly to dryness. This causes some of the arsenic to precipitate as sulfide but in a condition such that it is oxidized by 6-normal nitric acid to arsenic acid. To the concentrated solution obtained by evaporation, add 5 ml of 6-normal nitric acid and boil until the residue is entirely dissolved or only a little sulfur remains. Evaporate nearly to dryness, add 3 ml of ammonium hydroxide and filter if necessary. The arsenic is now present as ammonium arsenate. To the clear solution add magnesium nitrate reagent, stir vigorously, and allow the mixture to stand for some time. A white crystalline precipitate of magnesium ammonium arsenate shows that arsenic is present. Filter, wash the precipitate with a little water, and pour over it a mixture of 1 ml silver nitrate solution and 6 drops acetic acid. A dark red residue of silver arsenate confirms the conclusion that arsenic is present.

5. Dilute the solution from (1) with water to a volume of 55 ml, and saturate with hydrogen sulfide at about 90°. Pass the hydrogen sulfide through the hot solution for eight minutes, to precipitate antimony sulfide, Sb_2S_3. Filter and wash the precipitate with hot water. Test the filtrate for tin by (7).

6. Transfer the antimony sulfide precipitate to a small casserole, dissolve it in 5 ml of concentrated hydrochloric acid, heating if neces-

sary. Unless a clear solution is obtained, add 5 ml of water and filter, rejecting the residue. Evaporate the filtrate to about 2 ml, cool, and add a flat piece of bright, mossy tin. After ten minutes pour off the liquid, wash the metal in water, and examine it for a *black** residue of antimony. Pour upon it about 2 ml of freshly prepared sodium hypobromite solution.† Antimony, unlike arsenic, is undissolved by this treatment.

7. As a preliminary test to see whether any tin is likely to be present, add just 4 ml of concentrated ammonium hydroxide to the filtrate from § 5 and saturate with hydrogen sulfide. If no precipitate forms after ten minutes, it is unnecessary to test further for tin. If a precipitate is obtained, evaporate, without filtering, to a volume of 15 ml or farther if the sulfide has not dissolved. Add about 2 g of powdered antimony and boil gently for two minutes. Filter and add at once 2 ml of hydrochloric acid and a little mercuric chloride solution. A white or gray precipitate proves that tin is present.

NOTE

If the sulfide precipitate, obtained by acidifying the sodium polysulfide solution, consists chiefly of arsenic pentasulfide, it is best to dissolve the arsenic sulfide first by means of ammonium carbonate solution (p. 144). Then the residue of Sb_2S_5, SnS_2, and S can be examined for antimony and tin.

To detect the arsenic in the ammonium carbonate solution, add hydrochloric acid, which reprecipitates arsenic pentasulfide. Dissolve the sulfide as indicated in Table IV and confirm the arsenic test as described there.

Quiz Questions on H_2S Precipitation

1. Into what four classes can the reactions of qual. anal. be divided? Give an example of each.
2. If a sat. soln. of H_2S at 20° is approx. 0.1 molal, its primary ionization const. is 0.91×10^{-7}, and its secondary ionization const. is 1.2×10^{-15}, compute the value of $[H^+]^2 \times [S^{--}]$ in the satd. soln.
3. If the *Sp* of H_2S is 1.08×10^{-23}, compute the $[S]^{--}$ conc. in a molal soln. of H_2S which is 0.2 *N* in H^+.
4. If the *Sp* of PbS is 4.2×10^{-28} and a soln. contains 3×10^{-21} moles of S^{--}, compute the wt. of Pb^{++} in mg that must be present in 400 ml of a soln., which is 0.1 molal in H_2S, in order to form a ppt. of PbS.
5. A soln. contains 200 mg of Cu^{++}, 200 mg of Fe^{+++}, 150 mg of Cr as $Cr_2O_7^{--}$, and is 3 *N* in H^+. The vol. of the soln. is 400 ml, and H_2S is introduced until no further chemical reaction takes place. Write balanced equations expressing all the changes that take place and compute the normal concn. of H^+ after the pptn. and reduction are ended.
6. Give the formulas of all the substances which are likely to ppt. when a soln. 3 *N* in H^+ is saturated with H_2S.
7. The law of Henry states that the soly. of a gas in a liquid (with which it does not react chemically) is proportional to the pressure of the gas. How does this apply to the pptn. by means of H_2S with respect to (*a*) the use of an open beaker or a closed flask and (*b*) the use of pure H_2S or that of a mixt. of hydrogen and hydrogen sulfide?

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* A deposit of copper may be obtained here but is red or brown in color.

† Add NaOH solution, drop by drop, to 2 ml of saturated bromine water until the solution becomes colorless or yellow, then add as many drops more of sodium hydroxide solution.

8. Write balanced equations showing the action of H_2S on $KMnO_4$, $K_2Cr_2O_7$, and $FeCl_3$ in acid soln.

9. If a soln. of Bi^{+++} is diluted with water, a white ppt. of BiOCl is formed, but when H_2S is introduced, the ppt. changes to black Bi_2S_3. Would the same be true of a suspension of $Bi(OH)_3$? Assume the Sp of Bi_2S_3 to be 5×10^{-73} and that of $Bi(OH)_3$ to be of about the same order of magnitude as $Fe(OH)_3$, namely 1.2×10^{-36}.

10. From the Sp of ZnS (1.2×10^{-23}) and the Sp of H_2S (1.08×10^{-22}) compute the H^+ concn. which cannot be exceeded in pptn. of 1 mg. of Zn as ZnS.

Quiz Questions on Na_2S_2 Separation

1. Give formulas of all the sulfides of the Cu and Sn group which are (*a*) yellow, (*b*) black or brown, and (*c*) orange.

2. How much $Na_2S \cdot 9\ H_2O$ (mol. wt. 240), how much NaOH (mol. wt. 40) and how much S (at. wt. 32) should be taken to make 1 l of reagent which shall be 3 *N* in Na_2S, 1 *N* in NaOH, and 1 *N* in Na_2S_2 (formed by the action of Na_2S on S)?

3. What happens when Na_2S_2 reagent is treated with acid? Write the equation and show also what happens when Na_2HgS_2, Na_3AsS_4, Na_3SbS_4, and Na_4SnS_3 are treated with dil. acid.

4. How many ml of 3 *N* NH_4OH are necessary to dissolve 0.50 g of As_2S_3?

5. How does a sulfide ppt. of the Cu and Sn group behave when treated with $(NH_4)_2S_2$ reagent instead of Na_2S_2 reagent? When is it better to use the ammoniacal soln.?

6. Write balanced equations to show two stages in the hydrolysis of Na_2S. Why is NaOH added to the reagent? Why is sulfur dissolved in the soln.?

7. If a ppt. of sulfides is treated with 8 ml of Na_2S reagent which is 3 *N* in Na_2S, 1 *N* in NaOH, and 1 *N* in Na_2S_2, how much 6 *N* HCl should be necessary to cause complete repptn. of As_2S_3, Sb_2S_3 and SnS_2?

8. Compare the S^{--} concns. of 0.1 *N* H_2S soln., the same soln. after it has been treated with an equal vol. of 0.1 *N* HCl, and of 0.1 *N* H_2S diluted with an equal vol. of 0.1 *N* NaOH. The primary ionization const. of H_2S is about 0.9×10^{-7}, and for the secondary ionization the const. is about 1.2×10^{-14}.

9. How much Na_2S_2 reagent is necessary to dissolve 0.5 g of Sn present as SnS? The reagent is 1 *N* in Na_2S_2.

10. Write equations expressing the treatment of the sulfides of Bi, Cu, Sn and Sb with Na_2S_2 reagent.

Quiz Questions on Copper Group

1. Give in tabular form an outline for the anal. of the copper group, starting with the pptd. sulfides.

2. Compare the action of NaOH and of NH_4OH when separately added to solns. of Bi^{+++}, Cu^{++}, Cd^{++}, and Pb^{++}. Note the effect of an excess of reagent. Write balanced equations to illustrate your answers.

3. By means of the mass-action principle, explain (*a*) effect of a slight excess of H_2SO_4 on the soly. of $PbSO_4$, (*b*) action of NH_4AcO soln. on $PbSO_4$, (*c*) why CuS dissolves in hot dil. HNO_3 better than in more concd. HCl.

4. What vol. of 6 *N* H_2SO_4 is needed for the pptn. of 200 mg. of Pb^{++} as $PbSO_4$?

5. Write balanced equations for: (*a*) Formation of a ppt. contg. Bi by adding NH_4OH to a soln. (*b*) Action of NH_3 soln. on Cu^{++}. (*c*) Action of NH_3 soln. on dissolved Cd^{++}. (*d*) Preparation of $NaSnO_2$ soln. (*e*) Action of SnO_3^{--} on $Bi(OH)_3$ ppt. (*f*) Decolorization of $Cu(NH_3)_4^{++}$ soln. by adding KCN.

6. Compute the vol. of H_2S gas, measured dry at 20° C and 740 mm pressure, required to ppt. 0.500 g of Bi as Bi_2S_3 from an acid soln.

7. Write equations to show the action of hot, 3 *N* HNO_3 on a mixt. of HgS, CuS, and Bi_2S_3.

Quiz Questions on Tin Group

1. Write balanced equations to show: (*a*) Reaction between $HgCl_2$ and $SnCl_2$. (*b*) Action of NaBrO soln. on As. (*c*) Action of conc. HCl on Sb_2S_3. (*d*) Action of $Mg(NO_3)_2$ reagent on AsO_4^{---} soln. (*e*) Action of HAcO and $AgNO_3$ on the ppt. formed in (*d*). (*f*) Reaction of HCl and $KClO_3$ forming Cl_2. (*g*) Reaction of HCl and $KClO_3$ forming ClO_2.

2. Explain why metallic Fe ppts. Cu but not Cd from dil. acid solns. Mention 2 cases where the same principle is utilized in the anal. of the tin group, and write equations to illustrate.

3. Arrange the elements Sn, Pb and Zn in the order in which they occur in the reduction potential series. If Sb were replaced by Zn in the test for Sn, how would it be necessary to modify the procedure?

4. Reproduce the tabular outline of the procedure for analyzing the tin group.

5. How is the soly. of $MgNH_4AsO_4$ affected by (*a*) hydrolysis, (*b*) presence of excess NH_4OH, (*c*) presence of ammonium salt, and (*d*) presence of acid?

6. Write balanced equations for: (*a*) The action of NaBrO on As. (*b*) Action of concd. HCl on Sb_2S_3. (*c*) Dissolving HgS in Na_2S soln. (*d*) Detection of Sn.

7. Write equations illustrating the Marsh test for As.

8. Explain how you could tell the valence of As, Sb, and Sn in solns. of their salts. Write an equation to illustrate each method of distinguishing.

9. Write equations showing how, by the reactions used in the qual. scheme, (*a*) a stannous salt can be converted to a stannic compd. and *vice versa*, (*b*) a trivalent Sb compd. can be changed to a quinquevalent Sb compd. and *vice versa*, (*c*) tervalent As can be oxidized to quinquevalent As and *vice versa*.

10. Complete and balance the following equations:

(*a*) $HgS + KClO_3 + HCl \rightarrow$ (*b*) $As_2S_3 + NH_4OH \rightarrow$

(*c*) $H_3AsO_4 + Zn + H^+ \rightarrow$ (*d*) $SnCl_6^{--} + Sb \rightarrow$ (*e*) $As_2S_3 + KClO_3 + HCl \rightarrow$

GROUP III. AMMONIUM SULFIDE GROUP

ALUMINUM, CHROMIUM, IRON, ZINC, MANGANESE, NICKEL, COBALT*

ALUMINUM, Al. At. Wt. 26.97, At. No. 13

Density 2.70. M. P. 658.7°. B. P. 1800°

Occurrence. — Aluminum occurs very extensively in nature, principally in the form of silicates, of which the feldspars and micas with their decomposition products are important examples: Orthoclase (feldspar), $KAlSi_3O_8$; kaolin (decomposed feldspar), $H_4Al_2Si_2O_9$; muscovite (mica), $KH_2Al_3(SiO_4)_3$. Impure kaolin is called clay.

Among the most important minerals which contain aluminum may be mentioned cryolite, Na_3AlF_6; spinel, $MgAl_2O_4$, or magnesium aluminate, which crystallizes in the regular system and is isomorphous with magnetite, $FeFe_2O_4$, and chromite, $FeCr_2O_4$; alunite, $KAl_3(SO_4)_2(OH)_6$; aluminum hydroxide as hydrargillite, $Al(OH)_3$, monoclinic; bauxite, $H_4Al_2O_5$; and diaspore, $HAlO_2$, orthorhombic.

Corundum, Al_2O_3, is next to the diamond the hardest mineral. Pure, transparent corundum often has a beautiful color and is classed with the precious stones. Thus the ruby, sapphire, oriental emerald, oriental topaz, and amethyst are nearly pure corundum colored by a little foreign oxide. Emery is an intimate mixture of corundum, magnetite, and iron sulfide. True topaz is $Al_2(F,OH)_2SiO_4$, turquoise is $Al_2(OH)_3PO_4 \cdot H_2O$, and garnet is chiefly $Ca_3Al_2(SiO_4)_3$.

Preparation and Properties. — The metal takes its name from the Latin word *alumen* = alum, one of the first salts recognized. Aluminum is a white metal, very light and strong in comparison with its weight. It was first isolated by Oersted in 1824 but did not attain any commercial importance until the discovery of its preparation by the electrolysis of aluminum oxide dissolved in molten cryolite at about 1000°. As a conductor of heat it is about half as good as copper, and as a conductor of electricity it is about 60 per cent as good as copper on the basis of cross-sectional area but twice as good as copper on the weight basis. Aluminum in a fairly pure state is used for automobile parts, cooking utensils, and as a deoxidizer in the manufacture of steel. One of its most important alloys contains 92.5 per cent aluminum and 8 per cent copper. Duralumin contains about 94 per cent aluminum, 4.5 per cent copper, 0.75 per cent magnesium, and 0.75 per cent manganese. The current price of the metal is 20–25 cents per pound and about 1,700,000 tons of the ore are mined annually. Aluminum is only slightly attacked by exposure to the atmosphere. From the position of this element in the electromotive series (p. 46), the metal should be attacked readily by the atmosphere; the reason it is apparently unattacked has been proved due to its becoming coated with a thin, firmly adherent, protective layer of oxide.

Aluminum is trivalent in all its compounds; it forms only one oxide, Al_2O_3, which is amphoteric. The metal dissolves in acid to form an aluminum salt and in caustic alkali to form a soluble aluminate. Aluminum readily replaces the hydrogen of hydrochloric acid, but it dissolves less readily in dilute sulfuric acid and becomes passive when treated with nitric acid. One theory of the cause of passivity is the formation of a closely adherent oxide film.

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* The elements titanium and uranium were described here in earlier editions of this book, but it seems better to describe them in Part V, among the rarer metals.

The action of aluminum upon dilute hydrochloric acid and upon aqueous solutions of caustic alkali is expressed by the following ionic equations:

$$2\,Al + 6\,H^+ \rightarrow 2\,Al^{+++} + 3\,H_2\uparrow$$
$$2\,Al + 2\,OH^- + 2\,H_2O \rightarrow 2\,AlO_2^- + 3\,H_2\uparrow$$

These are the proper solvents for aluminum.

Aluminum salts are as a rule colorless, and those which are soluble in water show an acid reaction in aqueous solution, on account of their being hydrolyzed to a considerable extent. This explains the fact that on evaporating a solution of aluminum chloride in water we do not obtain aluminum chloride, but the insoluble oxide, or hydroxide:

$$AlCl_3 + 3\,HOH \rightleftarrows Al(OH)_3 + 3\,HCl$$

The property which aluminum possesses of forming alums is very characteristic. The alums are double salts of aluminum sulfate with the sulfates of potassium, cesium, rubidium, or ammonium, of the general formula $RAl(SO_4)_2 \cdot 12\,H_2O$, in which R represents one of the univalent metals just mentioned. Similar salts in which the aluminum is replaced by trivalent iron or chromium are also called alums. The alums crystallize in the regular system, usually in octahedrons. The common potassium alum is much less soluble in cold than in hot water. Thus 100 ml of water dissolve 10.7 g of alum at 15° C and 283 g at 100° C.

The sulfide of aluminum can be prepared only in the dry way. It is a pale yellow substance, which is decomposed hydrolytically even by cold water into hydrogen sulfide and aluminum hydroxide:

$$Al_2S_3 + 6\,HOH \rightarrow 3\,H_2S + 2\,Al(OH)_3$$

Aluminum hydroxide is amphoteric; toward strong acids it plays the part of a base, toward strong bases it acts as an acid.

Reactions in the Wet Way

1. **Ammonia** produces a gelatinous precipitate of aluminum hydroxide, which, as a colloid, is somewhat soluble in water, but insoluble in the presence of ammonium salts:

$$2\,Al^{+++} + 6\,NH_3 + 6\,H_2O \rightarrow 2\,Al(OH)_3 + 6\,NH_4^+$$

The property which the aluminum hydroxide shows of partly dissolving in water is common to all *colloidal* substances (cf. p. 64). When dissolved they are sometimes said to exist in the *hydrosol* condition, and when precipitated as *hydrogel*.

The hydrosol form of aluminum hydroxide can be converted into hydrogel *by the addition of salts*,* preferably ammonium salts. *If, therefore, we desire to precipitate aluminum from a solution by means of ammonia, we take care that ammonium chloride is present.*

The freshly precipitated aluminum hydroxide is readily soluble in dilute acids; but after standing some time in a salt solution, or after long boiling, it becomes more difficultly soluble, so that it is necessary to digest it with acid for a long time in order to bring it completely into solution.

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* This principle is illustrated by the technical process of "salting out" colloidal dyes from their solutions.

The solubility product of aluminum hydroxide is so small that it is precipitated by ammonia even in the presence of ammonium salt but, because of its amphoteric nature, it begins to dissolve if the p_H exceeds 9. Aluminum does not show a tendency to form soluble complex cations with ammonia.

2. **Alkali Hydroxides** produce the same precipitate as ammonia, which is, however, in this case soluble in excess of the reagent, forming an alkali aluminate:

$$Al^{+++} + 3\ OH^- \rightarrow \mathbf{Al(OH)_3}$$
$$\mathbf{Al(OH)_3} + OH^- \rightarrow AlO_2^- + 2\ H_2O$$

If dilute acid is added to a solution of an aluminate, there is formed at first a precipitate of aluminum hydroxide, which dissolves on further addition of acid:

$$AlO_2^- + H^+ + H_2O \rightarrow \mathbf{Al(OH)_3}$$
$$\mathbf{Al(OH)_3} + 3\ H^+ \rightarrow Al^{+++} + 3\ H_2O$$

The aluminates are also decomposed by boiling with an ammonium salt:

$$AlO_2^- + NH_4^+ + H_2O \rightarrow \mathbf{Al(OH)_3} + NH_3\uparrow$$

Aluminum hydroxide is soluble in neutral tartrates of the alkalies, so that in the presence of tartaric acid there will be no precipitation on the addition of ammonia. Consequently the aluminum is present in such a solution not as simple aluminum cations but chiefly as complex negative ions:

$$\mathbf{Al(OH)_3} + C_4H_4O_6^{--} \rightarrow C_4H_2(AlOH)O_6^{--} + 2\ H_2O$$

Many other organic hydroxy-acids and hydroxy-compounds, such as malic and citric acids, sugars, and starches, have the same effect of preventing the precipitation of aluminum hydroxide by ammonia.

3. **Alkali Acetates** produce no precipitation in cold neutral solutions, but, on boiling the solution, a very voluminous precipitate of basic *aluminum* acetate is formed:

$$Al^{+++} + 3\ C_2H_3O_2^- \rightarrow \underset{\text{Soluble}}{AlC_2H_3O_2)_3}\ \text{(in the cold)}$$

$$Al(C_2H_3O_2)_3 + 2\ HOH \rightleftarrows \mathbf{Al}\begin{cases}\mathbf{OH}\\ \mathbf{OH}\\ \mathbf{C_2H_3O_2}\end{cases} + 2\ HC_2H_3O_2\ \text{(on boiling)}$$

If the solution is allowed to cool, the basic aluminum acetate redissolves. To make the reaction take place completely from left to right the solution must be hot and contain sufficient alkali acetate to keep the hydrogen-ion concentration about 3×10^{-6} ($p_H = 5.5$. Cf. pp. 49, 51, and 54).

4. **Alkali Carbonates** precipitate aluminum hydroxide (hydrolysis):

$$2\ Al^{+++} + 3\ CO_3^{--} + 3\ HOH \rightarrow 2\ \mathbf{Al(OH)_3} + 3\ CO_2\uparrow$$

5. **Alkali Phosphates,** *e.g.*, Na_2HPO_4, give a gelatinous precipitate of aluminum phosphate:

$$2\ HPO_4^{--} + Al^{+++} \rightarrow \mathbf{AlPO_4} + H_2PO_4^-$$

or, on addition of ammonia:

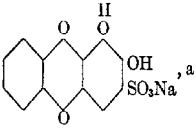
$$HPO_4^{--} + NH_3 + Al^{+++} \rightarrow \mathbf{AlPO_4} + NH_4^+$$

Aluminum phosphate is soluble in mineral acids, insoluble in acetic acid (differing from Ca, Sr, Ba, Mg), but readily soluble in sodium or potassium hydroxide solutions:

$$\mathbf{AlPO_4} + 4\ OH^- \rightarrow AlO_2^- + PO_4^{---} + 2\ H_2O$$

On boiling this alkaline solution (obtained in the last reaction) with ammonium chloride, a precipitate will be formed, consisting of a mixture of aluminum phosphate and aluminum hydroxide; barium chloride, on the contrary, will precipitate barium phosphate from such a solution and leave the aluminate dissolved.

6. **Alizarin,** $C_{14}H_6O_2(OH)_2$, in a freshly prepared 0.01 per cent solution which is 0.6-normal in acetic acid and 3-normal in sodium acetate, gives a red or pink color when a little of it is added to a fresh precipitate of aluminum hydroxide. If a large precipitate is to be tested, shake a little of the precipitate with filter paper pulp in a test tube and add about 3 ml of the alizarin reagent (Atack*).

Sodium alizarin sulfonate,  , a yellow dyestuff called Alizarin S, gives a red precipitate, or lake, corresponding to the formula $Al(C_{14}H_7O_4)_3$. The lake is formed in ammoniacal solutions and is stable toward acetic acid. The violet coloration produced by the action of OH^- on the excess of reagent disappears on adding the acid, and the color of the yellow dye reappears. To 1 drop of the solution of the aluminum salt which has been treated with an excess of NaOH to form the aluminate anion, AlO_2^-, add 1 drop of a 0.1 per cent solution of the yellow dye Alizarin S. Add acetic acid until the violet coloration disappears and 1 drop in addition. If aluminum is present (0.65 γ in 1 drop) a red coloration appears which increases on standing; a precipitate forms if much aluminum is present.

7. **Tincture of Alkanna** added to a neutral solution of an aluminum salt gives a reddish violet color with orange-yellow fluorescence. In a dilute solution, characteristic absorption bands are obtained in spectrum analysis.

8. **Aluminon,** a trade name for the ammonium salt of aurintricarboxylic acid, $C_{22}H_{14}O_9$, gives a bright red lake with aluminum salts. Similar, but brighter colored, lakes are formed with beryllium, yttrium, lanthanum, cerium, neodymium, erbium, zirconium, thorium, and possibly scandium. All these, except the beryllium and aluminum lakes, are dissolved or decolorized by adding a moderate excess of ammonium carbonate. This is perhaps the most sensitive test for aluminum ions that has ever been proposed and is best applied to a precipitate of $Al(OH)_3$ that is obtained in the usual scheme of analysis.

Dissolve the $Al(OH)_3$ precipitate in 5 ml of *N* HCl; add 5 ml of 3 *N* ammonium acetate solution and 5 ml of a 0.1 per cent aqueous aluminon solution. After mixing

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* *Chem. Zentr.*, **1916**, I, 176.

well, make the solution ammoniacal with a mixture of NH_4OH and $(NH_4)_2CO_3$. A bright red precipitate persisting in the ammoniacal solution denotes the presence of aluminum.

9. **Ammonium Sulfide** causes precipitation of the hydroxide:

$$2\,Al^{+++} + 3\,S^{--} + 6\,HOH \rightarrow \mathbf{2\,Al(OH)_3} + 3\,H_2S\uparrow$$

The aqueous solution of ammonium sulfide is in equilibrium with NH_4OH and H_2S formed by hydrolysis. There are, therefore, enough OH^- ions in a solution of ammonium sulfide to cause the precipitation of $Al(OH)_3$.

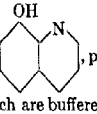
10. **Barium Carbonate,** suspended in water and added to the solution of an aluminum salt, also precipitates the hydroxide:

$$2\,Al^{+++} + 3\,\mathbf{BaCO_3} + 3\,HOH \rightarrow 3\,Ba^{++} + 3\,CO_2\uparrow + \mathbf{2\,Al(OH)_3}$$

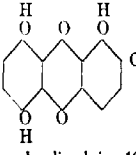
11. Ether precipitates white, crystalline aluminum chloride, $AlCl_3 \cdot 6\,H_2O$, from a concentrated solution which is saturated with HCl gas. Aluminum may be separated from beryllium in this way.

12. Morin, $C_{15}H_{10}O_7 \cdot 2\,H_2O$, the color principle of old fustic, a dyewood, gives a green fluorescence when added to a neutral or acetic acid solution containing Al; $Al(C_{15}H_9O_7)_3$ is formed. To detect aluminum in the presence of interfering ions, add an excess of NaOH to some of the solution, filter, take a drop of the solution on a black spot plate, acidify with 2 *N* $HC_2H_3O_2$, and add a drop of a saturated solution of morin in methyl alcohol. As little as 0.2 γ of aluminum will give the test (Feigl).

13. **Oxalic Acid** and its salts do not form precipitates in solutions of aluminum salts. This helps to distinguish aluminum from certain rare earths of this analytical group (cerium, lanthanum, neodymium, praseodymium, and erbium) as well as from the alkaline earths.

14. **Oxine,** which is the trivial name for 8-hydroxyquinoline,  , precipitates aluminum hydroxyquinolate from acetic acid solutions which are buffered with sodium acetate.

15. **Potassium Sulfate** added to a concentrated solution of an aluminum salt causes the formation of potash alum, $KAl(SO_4)_2 \cdot 12\,H_2O$. Crystals of similar alums can be formed with other elements of the alkali group, particularly rubidium and cesium. The last-mentioned element forms a difficultly soluble alum.

16. **Quinalizarin,** $C_{14}H_4O_2(OH)_2$, or  , is also a very sensitive reagent for aluminum. Prepare test paper by dissolving 10 mg of quinalizarin in 2 ml of pyridine, diluting with 20 ml of acetone and moistening ashless filter paper with the resulting solution. Place a drop of the solution to be tested on the test paper and hold it for a little while over the concentrated ammonia bottle and then over acetic acid fumes until the blue color of the ammonium salt of quinalizarin disappears and

the paper which has not been touched with the aluminum solution reassumes the brown color of free quinalizarin. If as much as 0.005 γ of aluminum is present in the drop of solution, the paper will assume a red-violet to reddish tint. Quinalizarin gives a blue coloration with beryllium ions which is the basis of another very sensitive test. The above test is useful for detecting aluminum in the presence of magnesium.

17. **Sodium Thiosulfate,** $Na_2S_2O_3$, completely precipitates the aluminum as hydroxide on boiling:

$$2\,Al^{+++} + 3\,S_2O_3^{--} + 3\,HOH \rightarrow 3\,S + 3\,SO_2\uparrow + 2\,Al(OH)_3$$

The sodium thiosulfate, being a salt of a weak acid, serves to neutralize the H^+ ions formed by the hydrolysis of the aluminum salt, and the free $H_2S_2O_3$ is so unstable that it breaks down into S and SO_2; equilibrium is disturbed by the precipitation of the $Al(OH)_3$ and S and by the escape of SO_2 gas.

DETECTION OF ALUMINUM IN THE PRESENCE OF ORGANIC SUBSTANCES WHICH PREVENT THE PRECIPITATION BY THE ABOVE REAGENTS

The presence of tartaric acid or other non-volatile, organic hydroxy-compound prevents precipitation with above reagents. To detect the presence of aluminum in such cases, add 5 to 10 g of ammonium acetate to the solution, heat to boiling, and treat with a fresh 2 per cent solution of tannin until the voluminous dirty-white or buff precipitate flocculates. The reaction is very delicate, but zirconium and thorium solutions give a similar precipitate. For the final identification of aluminum, the tannin precipitate should be filtered off, washed, ignited, and tested on charcoal with cobalt nitrate (p. 194).

A number of other elements react in the same manner with tannin in tartrate solution; precipitates of characteristic colors are obtained (see Cr, Fe, V, Ti, Ta, Nb).*

Treatment of Insoluble Alumina

When strongly heated, aluminum hydroxide loses water and forms the anhydride, Al_2O_3, which is scarcely soluble at all in hydrochloric and nitric acids. In hot, concentrated sulfuric acid, containing a little water, it will dissolve after long digestion. Ignited aluminum oxide, as well as native alumina in the form of the minerals corundum, ruby, sapphire, and emery, are most readily brought into solution by fusion with potassium pyrosulfate. The fusion is accomplished in the following way: Take twelve times as much fused potassium acid sulfate as there is oxide to get into solution and heat it by itself in a silica crucible over a small flame. The acid potassium sulfate melts readily, at about 300° C, gives off water (causing frothing), and becomes changed into potassium pyrosulfate:

$$2\,KHSO_4 \rightarrow H_2O + K_2S_2O_7$$

* Schoeller and Webb, *Analyst*, **54**, 709 (1929).

As soon as the frothing has ceased, the transformation into potassium pyrosulfate is complete. Add the dry aluminum oxide to the crucible and continue heating until the melt begins to solidify (showing that a considerable amount of potassium sulfate, which melts much more difficultly than the pyrosulfate, has been formed), then raise the temperature and continue heating until the oxide has dissolved clear in the melt. By heating the pyrosulfate, SO_3 is given off, which at the high temperature is very active:

$$K_2S_2O_7 \rightarrow K_2SO_4 + SO_3$$

If the heating is too rapid, much of the SO_3 is lost.

After the reaction is complete, the melt contains the aluminum as aluminum sulfate in the presence of potassium sulfate:

$$3\ K_2S_2O_7 + Al_2O_3 \rightarrow Al_2(SO_4)_3 + 3\ K_2SO_4$$

and both these substances are soluble in water.

The ignited aluminum oxide can also be brought into solution by fusion with caustic alkalies:

$$Al_2O_3 + 2\ KOH \rightarrow 2\ KAlO_2 + H_2O$$

This last operation is usually carried on in a silver crucible, never in platinum, which would be strongly attacked.

Reactions in the Dry Way

Aluminum compounds, on being heated with sodium carbonate on charcoal before the blowpipe, give a white, infusible, brightly glowing oxide, which, when moistened with cobalt nitrate solution and again heated, becomes a blue infusible mass (Thénard's blue):

$$Co(NO_3)_2 \rightarrow CoO + N_2O_5\uparrow$$
$$Al_2O_3 + CoO \rightarrow CoAl_2O_4$$

In carrying out this test it is extremely important not to use an excess of cobalt nitrate, for this salt leaves black cobalt oxide behind on ignition and when an excess is present it entirely obscures the blue color of cobaltous aluminate.

The test is usually applied to a precipitate of aluminum hydroxide. A good way to carry it out is as follows: Dissolve all or a part of the precipitate in 5 ml of 2 *N* HNO_3. Add 5–10 ml of water, 2–15 drops of 0.3 *N* $Co(NO_3)_2$ solution, and 3 ml of 6 *N* NH_4OH. Filter, wash the precipitate with water, and drain it as dry as possible with the aid of suction. Take up some of the precipitate with as little paper as possible in a loop of platinum wire, moisten the residue with 1 drop of concentrated sulfuric acid from a stirring rod, and heat at first carefully and finally very strongly. Silica, the substance most likely to be mis-

taken for alumina, gives a fusible, shiny mass of $CoSiO_3$, but alumina gives a dull, dark blue mass of $Co(AlO_2)_2$ which is infusible.*

All fused glasses, such as borax beads, sodium phosphate beads, etc., are colored blue by cobalt oxide. The blue color is also obtained with certain other infusible compounds containing no aluminum, *e.g.*, alkaline-earth phosphates.

Aluminum salts are not volatile, and do not color the flame. By ignition in the air, all aluminum salts, with the exception of the phosphate and silicate, are decomposed, leaving behind the oxide:

$$4\ AlCl_3 + 3\ O_2 \rightarrow 2\ Al_2O_3 + 6\ Cl_2$$
$$2\ Al(NO_3)_3 \rightarrow Al_2O_3 + 3\ N_2O_5$$
$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3\ SO_3$$

CHROMIUM, Cr. At. Wt. 52.01, At. No. 24

Density 7.138. M. P. 1600°. B. P. 2200°

Occurrence. — Chromium occurs in nature as chromite, $FeCr_2O_4$, isomorphous with spinel (see aluminum); as monoclinic crocoite, $PbCrO_4$; and as laxmannite, a double compound of lead-copper phosphate and basic lead chromate, $(Pb,Cu)_3(PO_4)_2 \cdot Pb_2O(CrO_4)_2$. Furthermore, it is found in small quantities in many silicates, such as muscovites, biotites, augites, etc., and consequently in their weathering products, as in many kaolins, bauxite, etc.

The Metal and Its Oxides. — The name *chromium* is derived from the Greek word *chroma* = color and is appropriate because most chromium salts are colored. The element was discovered by Vauquelin in 1798. It is a crystalline metal slightly more grayish than silver. When heated to 200–300° in the air it burns to Cr_2O_3. It is not a ductile metal and is non-magnetic. It finds considerable use in making alloy steels, many of which contain nickel. The so-called stainless steels contain 8–14 per cent chromium. Nichrome wire, containing about 80 per cent nickel and 20 per cent chromium, is used for resistance wire in electrical heating units and for the triangles for supporting crucibles in the chemical laboratory. Chromium plating has, to a considerable extent, replaced nickel plating as a protective coating for less resistant metals. The metal can be produced (*a*) by heating Cr_2O_3 with carbon, (*b*) by the Goldschmidt thermite process in which the oxide is heated with aluminum powder, (*c*) by fusing $CrCl_3$ with Zn, Cd, or Mg and KCl and NaCl as fluxes. It can also be produced by the electrolysis of aqueous solutions under suitable conditions.

Metallic chromium is easily reduced to powder. The metal dissolves in hydrochloric, hydrobromic, hydriodic, sulfuric, and oxalic acids with evolution of hydrogen and formation of chromous, or a mixture of chromous and chromic salts. The metal is easily made passive, however, by immersion in nitric acid or by anodic polarization. Passive chromium retains its luster in the air, is insoluble in dilute acids, and resembles the noble metals. With oxygen chromium forms the following oxides: chromous oxide, CrO; chromic oxide, Cr_2O_3; chromic acid anhydride, CrO_3; and chromium peroxides corresponding to CrO_4, Cr_2O_9, Cr_2O_{11}, and Cr_2O_{13} (cf. p. 202).

* Carl Otto, *J. Am. Chem. Soc.*, **48**, 1604 (1926).

The oxides CrO and Cr_2O_3 are basic anhydrides, and, on being dissolved in acids, yield the corresponding salts, the chromous and the chromic compounds. Chromium trioxide is the anhydride of the hypothetical chromic acid, H_2CrO_4, and forms chromates with bases. The chromium peroxides have never been obtained pure; salts of perchromic acid have been isolated and analyzed. (Cf. p. 203.)

I. Chromous Compounds

Chromous oxide is known only in the form of its hydroxide, $Cr(OH)_2$, which, on being dried, loses hydrogen and water, leaving behind chromic oxide:

$$2\ Cr(OH)_2 \rightarrow H_2 + H_2O + Cr_2O_3$$

Like chromous hydroxide, all chromous compounds are extremely unstable, being changed readily by contact with the air into chromic compounds. Only the *halogen* compounds, the *phosphate*, *carbonate*, and *acetate*, are known in the dry state; the sulfate only in solution. The acetate, $Cr(C_2H_3O_2)_2 \cdot H_2O$, is a reddish brown, crystalline substance, insoluble in water, but readily soluble in hydrochloric acid. This solution, as well as that of all chromous salts, absorbs oxygen with avidity, and is consequently used in gas analysis for the determination of oxygen in gas mixtures. Solutions of chromous compounds are obtained by the reduction of chromic compounds with zinc and acid out of contact with the air.

On account of the instability of these compounds the analytical chemist will rarely meet them and further description is unnecessary.

II. Chromic Compounds

All chromic compounds contain chromium as a trivalent element; they are colored either green or violet, and are as a rule soluble in water. The *oxide*, *hydroxide*, *phosphate*, *anhydrous chloride*, and *sulfate*, after being strongly heated in a stream of carbon dioxide gas, are insoluble in water. Violet chromium chloride, obtained in the dry way, is insoluble in acids; it dissolves readily in water containing a trace of chromous chloride, or in the presence of stannous chloride (tin and hydrochloric acid). By dissolving the grayish green chromic hydroxide in acids, green solutions are always obtained, which on long standing become greenish violet or violet, but on boiling become green again. Chromic sulfate forms, with sulfates of potassium, ammonium, cesium, or rubidium, the so-called chrome-alums, which crystallize in the regular system. These alums, like all other chromic salts, react acid in aqueous solution (hydrolysis).

Crystals are obtained by evaporation of the violet solutions; the green solutions either give uncrystallizable sirups or are changed into violet crystals. The addition of nitric acid favors the change of the green into the violet modification. The color changes are partly due to different states of hydration and partly to the formation of complex cations. Often the green salt contains a complex ion. Chromium shows a great tendency to form complex ions with hydrocyanic and sulfuric acids, organic compounds containing hydroxyl, and with ammonia, amines, pyridine, etc. These complex compounds do not show many of the characteristic chromium reactions.

Chromic sulfide, Cr_2S_3, can be obtained only in the dry way. On being treated with water it is decomposed quantitatively into hydroxide and hydrogen sulfide.

Reactions in the Wet Way

1. **Ammonia** produces a grayish green, gelatinous precipitate of chromic hydroxide:

$$Cr^{+++} + 3\,NH_4OH \rightarrow Cr(OH)_3 + 3\,NH_4^+$$

Chromic hydroxide is somewhat soluble in excess of ammonia, forming a violet or pink solution, particularly soluble when the ammonia is added to a *violet* solution of a chromic salt, in the presence of ammonium salts. This is caused by the formation of complex chromic-ammonia cations, which, however, may be decomposed by boiling the solution until the excess of ammonia has been driven off, when the chromium is quantitatively precipitated as hydroxide. In order, then, to precipitate the chromium from a solution as hydroxide, it is necessary to precipitate at a boiling temperature, and to use as little ammonia as possible.

By ignition of chromic hydroxide, green chromic oxide is obtained, which after strong ignition is insoluble in acids. In order to bring it into solution, it must be fused with potassium pyrosulfate (cf. aluminum, p. 193); or with an oxidizing flux such as sodium carbonate and potassium nitrate in a platinum crucible or sodium peroxide in a nickel or iron crucible, whereby sodium chromate is formed:

$$2\,Cr_2O_3 + 4\,Na_2CO_3 + 3\,O_2 \rightarrow 4\,Na_2CrO_4 + 4\,CO_2\uparrow$$

If the product of this last fusion is dissolved in water, acidified with hydrochloric acid, and boiled with alcohol, a green solution of chromic chloride will be obtained (p. 202), from which the chromium can be precipitated as hydroxide with ammonia. By fusing with sodium carbonate and potassium nitrate in a platinum crucible, the crucible will always be slightly attacked, so that a small amount of platinum will go into solution with the fused mass; it can be removed, after the treatment with hydrochloric acid, by passing hydrogen sulfide into the boiling solution, and filtering off the precipitated platinum sulfide.

2. **Alkali Acetates** produce no precipitation in solutions of chromic salts, even when the solutions are boiled. If, however, considerable amounts of aluminum and ferric salts are present at the same time, the chromium will be precipitated almost quantitatively with the iron and aluminum as basic acetate. If chromium predominates, only a part of the metals will be precipitated as basic salts; the filtrate will contain iron and aluminum with chromium. *In the presence of chromium, the basic acetate separation is always uncertain.*

3. **Alkali Carbonates, Barium Carbonate, Ammonium Sulfide,** and **Alkali Thiosulfates** precipitate chromic hydroxide, as with aluminum.

4. **Alkali Hydroxides** cause the same precipitation as ammonia; but the precipitate is readily soluble in excess of the reagent, forming a green chromite:

$$Cr^{+++} + 3\,OH^- \rightarrow Cr(OH)_3;\ Cr(OH)_3 + OH^- \rightleftarrows CrO_2^- + 2\,H_2O$$

Chromic hydroxide behaves here as a weak acid. The reaction is reversible, the presence of considerable water causing the reaction

to go from right to left, particularly at the boiling temperature. By boiling the dilute solution, complete hydrolysis takes place; the chromium is almost quantitatively precipitated as hydroxide (difference from aluminum).

Chromic hydroxide often causes coprecipitation of other bases as insoluble chromites, particularly zinc, alkaline earth, and magnesium.

The precipitation of chromic hydroxide, by any of the reactions here described, is also prevented by tartaric, citric, and oxalic acids and by sugar. Sometimes no precipitation at all is obtained, and the precipitation is always incomplete. Taninn produces a greenish precipitate when added to a boiling tartrate solution containing chromic salt and an excess of ammonium acetate.

5. **Alkali Phosphates** give a greenish, amorphous precipitate of chromic phosphate:

$$2\ HPO_4^{--} + Cr^{+++} \rightarrow \mathbf{CrPO_4} + H_2PO_4^-$$

Chromic phosphate is readily soluble in mineral acids and in cold acetic acid. On boiling the acetic acid solution, chromic phosphate separates out again. Oxalic acid prevents the precipitation of chromic phosphate owing to the formation of a complex chrome-oxalate ion.

6. **Hydrogen Peroxide.** See page 202.

7. **Hydrogen Sulfide** has no action upon an acid solution of chromic salt; the sulfide of chromium cannot be prepared except in the dry way and hydrolyzes in contact with water. In an alkaline solution containing chromite anions, hydrogen sulfide precipitates chromic hydroxide:

$$2\ CrO_2^- + H_2S + 2\ H_2O \rightarrow 2\ Cr(OH)_3 + S^{--}$$

Acid solutions of chromates and dichromates are reduced to chromic salt, and sulfur is precipitated (cf. p. 34).

8. **Sodium Peroxide** and caustic alkali added to the solution of a chromic salt convert the trivalent chromium into the chromate ion in which the chromium has a positive valence of six:

$$2\ Cr^{+++} + 3\ Na_2O_2 + 4\ OH^- \rightarrow 2\ CrO_4^{--} + 6\ Na^+ + 2\ H_2O$$

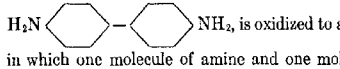
9. The following four tests, which depend upon the preliminary conversion of the chromic ions to chromate or dichromate anions, are useful for the detection of very small quantities of chromium in a single drop of solution. The silver chromate or lead chromate test is given with 6 γ of chromium, the diphenylcarbazide test with 0.25 γ of chromium in an alkaline solution and with 0.8 γ of chromium when the oxidation takes place in an acid solution, and the benzidine test is given with 0.25 γ of chromium.

(*a*) Place 1 drop of the solution to be tested on filter paper, add a drop of strong sodium hydroxide solution, and hold the paper over bromine vapors. Then add 1 drop of lead acetate or silver nitrate solution which is strongly acid with acetic acid. Yellow $PbCrO_4$ or red Ag_2CrO_4 is precipitated.

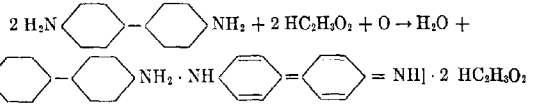
(*b*) Place a drop of the acid solution of chromic salt upon a spot plate; add 1 drop of saturated bromine water and 2–3 drops of 2 *N* NaOH solution. Make sure that the mixture is alkaline to litmus. Mix well with a stirring rod; add a tiny crystal of phenol, 1 drop of a 1 per cent solution of diphenylcarbazide in alcohol, and finally 2 *N* sulfuric acid, drop by drop, until the red coloration, produced by the reaction of the sodium hydroxide upon the diphenylcarbazide, disappears. Then, if chromium is present, a blue-violet coloration appears. If manganese or cobalt is present, the test is obscured by the black precipitates formed by the action of bromine and sodium hydroxide $Co(OH)_3$ and $MnO(OH)_2$.

(*c*) Place 1 drop of the acid solution to be tested upon a spot plate; add 1 drop of a saturated solution of alkali persulfate and 1 drop of 2 per cent silver nitrate solution. After two minutes add 1 drop of alcoholic diphenylcarbazide solution; a violet or pink coloration will appear if chromium is present. Manganese interferes with this test since purple MnO_4^- is formed by the persulfate oxidation. By the addition of a little sodium azide MnO_4^- is reduced and the chromium test appears.

(*d*) Place 1 drop of a fairly strong and freshly prepared aqueous solution of sodium peroxide upon filter paper and cover this with a drop of the solution to be tested. The CrO_4^{--} formed will be drawn by capillary attraction to the outer zone of the spot and can be detected there by adding a drop of a solution of benzidine in acetic acid. A blue ring of *benzidine blue* is formed. Benzidine, $C_{12}H_8(NH_2)_2$ or



in which one molecule of amine and one molecule of imine are combined with two equivalents of acid:



Precautions must be taken in applying the test when vanadium or manganese is present.

III. Chromates

Chromium trioxide, CrO_3, forms red orthorhombic needles, which dissolve readily in water to an orange-red solution. If this solution is neutralized with potassium hydroxide, it becomes yellow, and on evaporation yellow K_2CrO_4, the potassium salt of chromic acid, H_2CrO_4, is obtained. If the yellow solution of potassium chromate is acidified, and then allowed to crystallize, orange-red prisms of triclinic potassium dichromate crystals, $K_2Cr_2O_7$, are formed.

The aqueous solution of potassium chromate, K_2CrO_4, contains colorless potassium ions and yellow CrO_4^{--} anions; the aqueous solution of potassium dichromate, $K_2Cr_2O_7$, contains, in the presence of the colorless potassium ions, the orange-red $Cr_2O_7^{--}$ anions:

$$K_2Cr_2O_7 \rightleftarrows 2\ K^+ + Cr_2O_7^{--}$$

We are able, therefore, to determine from the color of a chromate solution the nature of the chromate ion which is present.

The free acids, H_2CrO_4 and $H_2Cr_2O_7$, cannot be isolated, but only the corresponding anhydride, CrO_3, which is very soluble in water. When chromium trioxide dissolves in water, the following reaction takes place: $CrO_3 + H_2O \rightleftarrows H_2CrO_4$.

The first hydrogen of this acid belongs to the class of very strong acids (cf. p. 11) and consequently the greater part of the H_2CrO_4 undergoes ionization as fast as it is formed: $H_2CrO_4 \rightleftarrows H^+ + HCrO_4^-$. The second hydrogen, on the other hand, corresponds to that of a very weak acid, and we may say that in the presence of hydrogen ions $HCrO_4^-$ is scarcely ionized at all. The $HCrO_4^-$, however, enters into the following equilibrium: $2\ HCrO_4^- \rightleftarrows H_2O + Cr_2O_7^{--}$. The presence of hydrogen ions favors the formation of the dichromate ion, and the presence of OH^- ions will cause dichromate ions to disappear and yellow CrO_4^{--} ions to take their place:

$$Cr_2O_7^{--} + 2\ OH^- \rightarrow 2\ CrO_4^{--} + H_2O$$

Remark. — Although we may judge as to the color of the ions from the color of the solution, and often predict what the color of the solid salt will be, yet, on the other hand, we cannot tell what the color of the solution will be from that of the salt itself. Yellow lead iodide dissolves in water to a colorless solution, and the yellow and red iodides of mercury, although only slightly soluble, also do not yield colored solutions.

If the solution of a salt is colored, the salt itself is usually colored; but the reverse is not always true.

All chromates are insoluble in water, except those of the alkalies, calcium, strontium, and magnesium. All chromates dissolve in nitric acid, except fused lead chromate, which dissolves with difficulty.

Formation of Chromates

All chromium compounds may be readily oxidized to chromates. According to whether the compound is soluble in water or not, different methods are used to effect the oxidation.

The student should not attempt to memorize a large number of chemical equations, but he should strive to become able to express his chemical knowledge in the form of equations or equilibrium expressions. To balance equations representing the oxidation of chromium, it should be remembered that the chromium is changed from a positive valence of three (in the form of chromic cations or chromite anions) to a positive valence of six (in the form of chromic acid, chromate, or dichromate ions). When the oxidation takes place by means of halogen, a halide is formed and the halogen is changed from the neutral condition to the form of a negative ion with unit charge. When hypochlorite is the oxidizing agent, the unit positive charge on the chlorine atom is lost and a unit negative charge takes its place, which corresponds to the loss of two positive charges. Similarly, lead peroxide and hydrogen peroxide have an oxidizing power corresponding to the loss of two unit charges of positive electricity.

The valence of the chromium in the anions CrO_2^-, CrO_4^{--}, and $Cr_2O_7^{--}$ is found, in accordance with the rule given on page 28, by subtracting the charge of the ion from the product obtained by multiplying the number of oxygen atoms present in the ion by its valence of two. In equilibrium expressions it is important to make sure that the algebraic sum of the positive and negative charges on one side is exactly the same as the algebraic sum of the charges on the other. With a little practice it is very easy to determine whether hydrogen ions, hydroxide ions, or water molecules are required to make the equation balance.

Oxidation in alkaline solutions is effected:

(*a*) By halogens. If sodium or potassium hydroxide is added in excess to a solution of a chromic salt, and chlorine or bromine is conducted into the solution, the

oxidation will be complete in a few minutes: the green chromite becomes yellow chromate:

$$2\ CrO_2^- + 8\ OH^- + 3\ Cl_2 \rightarrow 2\ CrO_4^{--} + 6\ Cl^- + 4\ H_2O$$

Chromic compounds can also be oxidized by halogens in the presence of sodium acetate, the reaction going extremely slowly in the cold, but very quickly on warming:

$$2\ Cr^{+++} + 3\ Cl_2 + 8\ H_2O \rightarrow 2\ CrO_4^{--} + 6\ Cl^- + 16\ H^+$$

The sodium acetate greatly lowers the concentration of the hydrogen ions and causes the reaction to proceed from left to right (cf. p. 49).

(*b*) By hypochlorites (sodium hypochlorite, chloride of lime, etc.):

$$2\ CrO_2^- + 3\ OCl^- + 2\ OH^- \rightarrow 2\ CrO_4^{--} + 3\ Cl^- + H_2O$$

(*c*) By lead peroxide. The alkaline solution is boiled with lead peroxide:

$$2\ CrO_2^- + 3\ PbO_2 + 8\ OH^- \rightarrow 3\ PbO_2^{--} + 2\ CrO_4^{--} + 4\ H_2O$$

(*d*) By hydrogen peroxide,

$$2\ CrO_2^- + 3\ H_2O_2 + 2\ OH^- \rightarrow 2\ CrO_4^{--} + 4\ H_2O$$

the reaction taking place on warming.

(*e*) By freshly precipitated manganese dioxide. The oxidation takes place on boiling the neutral or slightly acid solution:

$$2\ Cr^{+++} + 3\ MnO_2 + 4\ OH^- \rightarrow 2\ CrO_4^{--} + 3\ Mn^{++} + 2\ H_2O$$

It is evident from this last equilibrium expression that the presence of hydroxide ions should favor the oxidation and hydrogen ions should hinder it. On the other hand, manganese dioxide is very insoluble in alkaline solutions. It is necessary, therefore, to have the solution neutral or slightly acid in order to obtain a sufficient concentration of quadrivalent manganese in solution.

In acid solutions the chromic cation is the most stable condition for chromium, but in alkaline solutions the chromate anion is the more stable condition. In acid solutions, therefore, it is easy to reduce a chromate to chromic salt, and in alkaline solutions it is easy to oxidize a chromic salt to chromate.

Oxidation in acid solution may be effected by boiling with very energetic oxidizing agents such as concentrated nitric acid and potassium chlorate, sodium bismuthate (or bismuth tetroxide), or potassium permanganate:

$$2\ Cr^{+++} + 3\ NaBiO_3 + 4\ H^+ \rightarrow Cr_2O_7^{--} + 3\ Na^+ + 3\ Bi^{+++} + 2\ H_2O$$

In carrying out this reaction the chloride should not be used, or any other salt of which the anion is capable of oxidation; the acid used should be nitric or sulfuric acid.

Oxidation in acid solution is accomplished very easily by alkali persulfate if a little silver ion is present as catalyst. The silver ion presumably forms unstable bivalent silver ion or an unstable silver peroxide:

$$2\ Cr^{+++} + 3\ S_2O_8^{--} + 7\ H_2O \rightarrow Cr_2O_7^{--} + 6\ SO_4^{--} + 14\ H^+$$

With an insoluble chromium compound, such as strongly ignited chromic oxide, or the mineral chromite, the oxidation is effected by means of fusion with sodium carbonate and an oxidizing agent such as potassium nitrate, potassium chlorate, or sodium peroxide (cf. pp. 197, 200). The alkali chromates thus obtained are of a deep yellow color, and are readily soluble in water.

Reduction of Chromates

Chromic acid, chromates, and dichromates are strong oxidizing agents in acid solutions. The oxidations take place even in very dilute solution, and for this reason potassium dichromate is often used in quantitative analysis, the quantity of reducing agent being determined by the volume of potassium dichromate required to react with it. Ferrous ions, sulfurous acid, hydrogen sulfide, and hydriodic acid are oxidized at ordinary temperatures. Oxalic acid and alcohol are oxidized slowly at the laboratory temperature and very quickly on heating the solution; hydrochloric acid and hydrobromic acid only when the solution is hot. The original orange solution is changed to green, the color of chromic ions:

$$Cr_2O_7^{--} + 6\ Fe^{++} + 14\ H^+ \rightarrow 2\ Cr^{+++} + 6\ Fe^{+++} + 7\ H_2O$$
$$Cr_2O_7^{--} + 3\ SO_3^{--} + 8\ H^+ \rightarrow 2\ Cr^{+++} + 3\ SO_4^{--} + 4\ H_2O$$
$$Cr_2O_7^{--} + 3\ H_2S + 8\ H^+ \rightarrow 2\ Cr^{+++} + 3\ S + 7\ H_2O$$
$$Cr_2O_7^{--} + 3\ H_2C_2O_4 + 8\ H^+ \rightarrow 2\ Cr^{+++} + 6\ CO_2\uparrow + 7\ H_2O$$
$$Cr_2O_7^{--} + 6\ I^- + 14\ H^+ \rightarrow 2\ Cr^{+++} + 3\ I_2 + 7\ H_2O$$
$$Cr_2O_7^{--} + 6\ HCl + 8\ H^+ \rightarrow 2\ Cr^{+++} + 3\ Cl_2\uparrow + 7\ H_2O$$

Since this last reaction takes place only on warming, it furnishes us with a convenient method for preparing small quantities of chlorine for analytical purposes, because the evolution of chlorine ceases as soon as the lamp is taken away. It is necessary, however, to employ an excess of hydrochloric acid, for otherwise no chlorine will be evolved owing to the formation of potassium chlorochromate, $KCrO_3Cl$:

$$Cr_2O_7^{--} + 2\ HCl \rightarrow 2\ CrO_3Cl^- + H_2O$$

which is decomposed on adding more hydrochloric acid:

$$2\ CrO_3Cl^- + 4\ HCl + 8\ H^+ \rightarrow 2\ Cr^{+++} + 6\ H_2O + 3\ Cl_2\uparrow$$

If alcohol and hydrochloric acid are allowed to act simultaneously upon a chromate (the reaction takes place on gentle warming without the evolution of chlorine), the alcohol is oxidized to aldehyde:

$$Cr_2O_7^{--} + 3\ C_2H_5OH + 8\ H^+ \rightarrow 2\ Cr^{+++} + 7\ H_2O + 3\ \underset{\text{Aldehyde}}{CH_3CHO}$$

This last reaction is often used for reducing a chromate, because the aldehyde (recognizable by its peculiar acrid odor) and the excess of alcohol are easily removed by boiling the solution, which then contains simply the chromium and the metal of the chromate as chlorides.

By boiling chromates with concentrated sulfuric acid, reduction takes place with evolution of oxygen:

$$2\ K_2Cr_2O_7 + 8\ H_2SO_4 \rightarrow 2\ K_2SO_4 + 2\ Cr_2(SO_4)_3 + 8\ H_2O + 3\ O_2\uparrow$$

Perchromic Acids

The behavior of *free chromic acid* toward *hydrogen peroxide* is characteristic. The chromic acid is converted into blue perchromic acids which are soluble in ether: H_7CrO_{10}, H_3CrO_7, or H_3CrO_8.

If a *cold, alkaline* solution of a chromate is treated with neutral hydrogen peroxide, the solution is colored red, owing to the formation of an alkali salt of perchromic acid, H_3CrO_8:

$$2\ K_2CrO_4 + 7\ H_2O_2 + 2\ KOH \rightarrow 8\ H_2O + 2\ K_3CrO_8$$

Little by little the red color disappears, with evolution of oxygen, and the yellow color of the chromate returns:

$$4\ K_3CrO_8 + 2\ H_2O \rightarrow 4\ KOH + 4\ K_2CrO_4 + 7\ O_2\uparrow$$

If a *cold, neutral* solution of potassium dichromate is treated with hydrogen peroxide, the solution is colored violet, owing to the formation of the potassium salt of a slightly different perchromic acid, H_3CrO_7:

$$K_2Cr_2O_7 + 5\ H_2O_2 \rightarrow 3\ H_2O + 2\ KH_3CrO_7$$

Again, the violet color gradually disappears with evolution of oxygen and regeneration of the dichromate:

$$4\ KH_3CrO_7 \rightarrow 2\ K_2Cr_2O_7 + 5\ O_2\uparrow + 4\ H_2O$$

If either the red or violet solution, obtained as above described, is shaken with ether, the ether remains colorless.

The behavior of chromate solutions toward an excess of hydrogen peroxide in the presence of dilute sulfuric acid is quite different. There is then formed invariably the perchromic acid richest in oxygen, H_7CrO_{10}, and the solution is turned an intense blue. The blue color disappears after a short time and the solution turns green, owing to the conversion of all the chromium into the chromic condition:

$$2\ H_7CrO_{10} + 3\ H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 10\ H_2O + 5\ O_2\uparrow$$

This perchromic acid is very soluble in ether; if, therefore, the aqueous solution is shaken with ether, the ether becomes colored a beautiful blue. In fact, this acid is more stable in ethereal than in aqueous solution.

Since the formation of the intensely blue perchromic acid takes place so readily, it may be used as a basis for a sensitive test for free chromic acid, which is made as follows: Add a few drops of dilute sulfuric acid to 1 or 2 ml of hydrogen peroxide and shake with 2 ml of ether; then add a little of the chromate solution and shake the mixture again. In the presence of 0.1 mg of chromic acid, the upper ether layer is colored intensely blue, and the reaction is noticeable with only 0.007 mg of chromic acid (Lehner).

Most chromates are insoluble in water, and exhibit characteristic colors; therefore it is easiest to test for chromium when it is present as a chromate. The test for oxidizing constituents with $MnCl_2$ in concentrated hydrochloric acid (cf. p. 225) is easily obtained with a chromate.

Reactions for the Precipitation of Chromic Acid

1. **Sulfuric Acid.** — *Dilute* sulfuric acid causes, at the most, a change of color from yellow to orange, without any evolution of gas.

Concentrated sulfuric acid causes the cold solution to change to orange color, and there is often a separation of red needles of CrO_3; the solution on being heated becomes green, the chromic acid being reduced to chromic salt with evolution of oxygen:

$$4\ CrO_3 + 6\ H_2SO_4 \rightarrow 6\ H_2O + 3\ O_2\uparrow + 2\ Cr_2(SO_4)_3$$

2. **Silver Nitrate** produces in neutral chromate solutions a brownish red precipitate of silver chromate:

$$CrO_4^{--} + 2\ Ag^+ \rightarrow Ag_2CrO_4$$

soluble in ammonia and mineral acids (hydrochloric acid changes it into insoluble silver chloride and chromic acid), insoluble in acetic acid. If, to a moderately concentrated solution of potassium dichromate, silver nitrate is added, a reddish brown precipitate of silver dichromate is formed:

$$Cr_2O_7^{--} + 2\,Ag^+ \rightarrow \mathbf{Ag_2Cr_2O_7}$$

which, on being boiled with water, is changed into the less soluble normal silver chromate:

$$2\,\mathbf{Ag_2Cr_2O_7} + H_2O \rightarrow 2\,\mathbf{Ag_2CrO_4} + H_2Cr_2O_7$$

The presence of sodium acetate causes this change to take place in the cold (cf. pp. 49, 102 and 103).

3. **Barium Chloride** produces in solutions of normal chromates a yellow precipitate of barium chromate:

$$CrO_4^{--} + Ba^{++} \rightarrow \mathbf{BaCrO_4}$$

soluble in mineral acids, insoluble in acetic acid. From solutions of dichromates the precipitation is complete only on addition of an alkali acetate (cf. p. 204).

4. **Lead Acetate** produces in solutions of normal chromates and dichromates a yellow precipitate of lead chromate, which is soluble in nitric acid but insoluble in acetic acid:

$$CrO_4^{--} + Pb^{++} \rightarrow \mathbf{PbCrO_4}$$

$$Cr_2O_7^{--} + 2\,Pb(C_2H_3O_2)_2 + H_2O \rightarrow 2\,HC_2H_3O_2 + 2\,C_2H_3O_2^- + 2\,\mathbf{PbCrO_4}$$

If lead nitrate is used instead of lead acetate, the precipitation is not complete unless sodium acetate is added.

5. **Mercurous Nitrate** produces in the cold a brown, amorphous precipitate of mercurous chromate:

$$CrO_4^{--} + Hg_2(NO_3)_2 \rightarrow \mathbf{Hg_2CrO_4} + 2\,NO_3^-$$

which on being boiled becomes fiery red and crystalline.

Behavior of Chromium Trioxide and Chromates on Ignition

Chromium Trioxide is decomposed on ignition into chromic oxide and oxygen, $4\,CrO_3 \rightarrow 2\,Cr_2O_3 + 3\,O_2\uparrow$. The chromates of ammonium and mercury behave quite similarly. Thus *normal ammonium chromate* on ignition is changed to *chromic oxide, ammonia, nitrogen,* and *water.* The reduction of the chromate is favored by the reducing action of ammonia which is present in excess:

$$2\,(NH_4)_2CrO_4 \rightarrow 2\,NH_3\uparrow + N_2\uparrow + 5\,H_2O\uparrow + Cr_2O_3$$

Ammonium Dichromate evolves only water and nitrogen:

$$(NH_4)_2Cr_2O_7 \rightarrow 4\ H_2O\uparrow + N_2\uparrow + Cr_2O_3$$

This decomposition takes place violently with scintillation. The chromic oxide which remains behind is very voluminous and reminds one of tea-leaves; consequently it is sometimes called "tea-leaved chromic oxide."

Mercurous Chromate is decomposed on ignition into *chromic oxide, mercury vapors,* and *oxygen*:

$$4\ Hg_2CrO_4 \rightarrow 2\ Cr_2O_3 + 8\ Hg\uparrow + 5\ O_2\uparrow$$

The Dichromates of the Alkalies are changed on ignition into normal chromates, chromic oxide, and oxygen:

$$4\ K_2Cr_2O_7 \rightarrow 4\ K_2CrO_4 + 2\ Cr_2O_3 + 3\ O_2\uparrow$$

Reactions in the Dry Way

All chromium compounds color borax and salt of phosphorus beads an emerald green both in the oxidizing and reducing flames. Heated with sodium carbonate on charcoal before the blowpipe, all chromium compounds yield a green slag, which after long heating is changed to green infusible chromic oxide. By fusing with sodium carbonate and potassium nitrate in the loop of a platinum wire, all chromium compounds yield a yellow melt of alkali chromate:

$$2\ Cr_2O_3 + 4\ Na_2CO_3 + 3\ O_2 \rightarrow 4\ Na_2CrO_4 + 4\ CO_2\uparrow$$

If the fused mass is dissolved in water and acidified with acetic acid, the solution will give with silver nitrate a reddish brown precipitate of silver chromate. This reaction is very delicate and serves for the detection of minute traces of chromium. Cloth which has been dyed with a chromium mordant can be tested in this way; the ash from a thread 5 cm long is sufficient to give the test.

IRON, Fe. At. Wt. 55.84, At. No. 26

Density 7.93 ± 0.03. M. P. about 1553° ± 1°. B. P. 2450° ± 50°

Occurrence. — Native iron is rarely found. It occurs in basaltic rocks; also in meteorites, associated with nickel, cobalt, carbon, sulfur, and phosphorus.

The most important iron ores are the oxides and sulfides. Of these may be mentioned:

Hematite, Fe_2O_3, isomorphous with corundum; magnetite, Fe_3O_4, isomorphous with spinel; goethite, $FeHO_2$, isomorphous with diaspore and manganite; limonite, $Fe_4H_6O_9$; (bog ore), $Fe(OH)_3$, which is used in the purification of illuminating gas; pyrite, FeS_2, which crystallizes in the isometric system; marcasite, FeS_2, orthorhombic. Iron disulfide is, therefore, dimorphous. Other important iron ores are siderite, $FeCO_3$, which is rhombohedral; vivianite, $Fe_3(PO_4)_2 \cdot 8\ H_2O$, is monoclinic.

The Metal and Its Alloys. — The element iron was known in prehistoric ages (before 4000 B.C.). The symbol is taken from the Latin name, *ferrum*. The German name is *Eisen*, which is similar to the Anglo-Saxon *isen*. Pure iron, which can be obtained by electrolysis or by heating pure iron salts in hydrogen, is silvery white and capable of taking a high polish. It is ductile, and the hardest of ductile metals; its tenacity is surpassed only by cobalt and nickel. Finely divided iron will burn in the air. Wrought iron contains less than 0.2 per cent carbon and is, with respect to the carbon content, like a very mild steel. The iron alloys with less than about 1.7 per cent of carbon are called steel, and those with more carbon, cast iron; but the names steel, cast iron, malleable iron, wrought iron, ingot iron, and pig iron are more or less determined by the method of manufacture. Steel always contains small quantities of elements other than carbon, especially manganese, phosphorus, sulfur, and silicon; care is taken to keep the content of the last three elements very small. The so-called *alloy* steels may contain appreciable quantities of nickel, chromium, vanadium, tungsten, or other elements. Cast irons contain more sulfur and silicon than most steels. The properties of steel or cast iron are determined partly by the chemical composition and largely by the heat treatment. Thus a given sample of steel may be very hard if it is cooled rapidly (quenched) from a high temperature, but the same sample will be relatively soft if it is allowed to cool slowly (annealed). A sample of cast iron containing a certain percentage of carbon may be very hard and brittle if the carbon is present as Fe_3C, or it may be much softer and less brittle if the carbon is present in the graphitic state. Silicon tends to cause the Fe_3C to break down into Fe + graphite, and sulfur tends to stop this decomposition. The composition of steel is controlled very carefully by chemical analysis and by examination of polished and etched specimens under the microscope (metallographic analysis). By microscopic examination it is possible not only to estimate, in many cases, the approximate carbon content of a sample of steel but also to determine the heat treatment to which the steel has been subjected. The microscope also reveals the presence of impurities, such as a little manganese sulfide or metal oxide, which cause flaws in the metal and may result in its failure to stand up under stress or strain. Such inclusions in the metal are also revealed by x-ray analysis which is often made in large steel laboratories. Because of its importance and wide usage, which results in the average production of more than 60,000,000 tons a year in the United States alone, iron has been studied more than almost any other element.

On dissolving commercial iron or steel in acids (H_2SO_4, HCl), hydrogen, and small amounts of hydrocarbons, hydrogen sulfide, mercaptans, phosphine, and silicon hydride are evolved, and these impurities give to the gas its unpleasant odor. Often an undissolved residue consisting chiefly of carbon remains.

The result of the action of nitric acid upon metallic iron depends upon the concentration of the acid and the temperature. With dilute nitric acid the reaction may take place without evolution of gas and with the formation of ferrous and ammonium ions:

$$4\,Fe + 10\,H^+ + NO_3^- \rightarrow 4\,Fe^{++} + NH_4^+ + 3\,H_2O$$

When the nitric acid is more concentrated, ferric ions are formed and nitrous oxide, or, with strong acid, nitrogen peroxide is evolved:

$$Fe + 4\,HNO_3 \rightarrow Fe(NO_3)_3 + 2\,H_2O + NO\uparrow$$
$$Fe + 6\,HNO_3 \rightarrow Fe(NO_3)_3 + 3\,H_2O + 3\,NO_2\uparrow$$

Cold, concentrated nitric acid makes iron passive; in this condition it does not react

with cold, dilute nitric acid or deposit copper from the aqueous solution of a cupric salt.

Iron is bivalent, trivalent, and rarely hexavalent, forming the following oxides:

Iron protoxide or ferrous oxide	Iron sesquioxide or ferric oxide	Ferrous-ferric oxide or magnetite	Iron trioxide
FeO	Fe_2O_3	Fe_3O_4	(FeO_3)

Iron trioxide, FeO_3, containing hexavalent iron, has never been isolated. It plays the part of an acid anhydride in ferrates of the general formula R_2FeO_4 which are decomposable by water. In this formula R represents a univalent metal. Fe_3O_4 is probably a ferrous ferrite, $Fe\begin{matrix}\diagup O - Fe = O \\ \diagdown O - Fe = O\end{matrix}$, rather than a mixture of Fe_2O_3 and FeO. Other ferrites such as $CaFe_2O_4$, $BaFe_2O_4$, $MgFe_2O_4$, and $ZnFe_2O_4$ are known.

By dissolving the three known oxides in acid the corresponding salts are obtained: thus ferrous oxide gives, with hydrochloric acid, ferrous chloride,

$$FeO + 2\,HCl \rightarrow H_2O + FeCl_2$$

ferric oxide gives ferric chloride,

$$Fe_2O_3 + 6\,HCl \rightarrow 3\,H_2O + 2\,FeCl_3$$

while ferrous-ferric oxide yields a mixture of ferrous and ferric chlorides:

$$Fe_3O_4 + 8\,HCl \rightarrow 4\,H_2O + 2\,FeCl_3 + FeCl_2$$

Iron, therefore, forms two series of salts: first, the ferrous, derived from ferrous oxide, containing bivalent iron; second, the ferric, derived from ferric oxide, containing trivalent iron. These two series of salts show a quite different behavior toward reagents.

The salts of bivalent iron (ferrous salts) are white when anhydrous but are greenish with water of crystallization; the solutions are colorless when dilute and greenish when concentrated. Ferrous salts are oxidized somewhat by exposure to the air and in solution they are oxidized by dissolved oxygen; this results in the formation of a basic salt, *e.g.*:

$$4\,FeSO_4 + O_2 \rightarrow 2\,Fe_2O(SO_4)_2$$

or

$$4\,FeSO_4 + O_2 + 2\,H_2O \rightarrow 4\,Fe\begin{matrix}\diagup OH \\ \diagdown SO_4\end{matrix}$$

The position of iron in the potential series shows that it is capable of being oxidized by hydrogen ions and suggests the possibility of its being oxidized to a measurable extent by the hydrogen ions of water. Careful experiments have shown that absolutely pure water containing no dissolved oxygen does not affect iron appreciably at ordinary laboratory temperatures, though there is evidence that a trace of iron dissolves and a film of hydrogen is formed on the metal which acts as a check upon further attack. The position of ferrous iron in the voltage series shows that hydrogen ions cannot oxidize iron appreciably to the ferric condition. The presence of dissolved oxygen, and this is normally present in all water that is exposed to the atmosphere, can accomplish this oxidation of the ferrous ions to the ferric condition and it also aids in the oxidation of the iron from the metallic to the ferrous state. In this way iron exposed to moisture and oxygen oxidizes or *rusts*. The rusting process is favored by the contact of the metal with a more noble metal, such as platinum, copper, or nickel; an electric couple is formed and the iron becomes the positive pole, so that the hydrogen set free by the action of iron upon water is deposited upon

the more noble metal. The presence of a more reactive metal, such as zinc, tends to hinder the corrosion of iron; the zinc corrodes instead of the iron.

The presence of an acid is, therefore, not absolutely necessary to start the corrosion of iron. An increase in the concentration of hydrogen ions, however, will greatly hasten the solution of the metal. When carbonic acid is present, ferrous bicarbonate is first formed, and, when the ferrous iron is oxidized to the ferric condition, the carbonic acid is set free again because ferric carbonate does not exist. The acid again acts upon the metal, and the rate of its corrosion is greatly accelerated.

Certain substances tend to make iron *passive*, particularly strong nitric acid. Passive iron does not dissolve in dilute nitric acid and does not corrode readily (cf. aluminum, p. 188). On the other hand, certain substances can overcome the passive condition and are said to *activate* the iron. Thus a solution of common salt is an activating agent.

Different varieties of iron and steel corrode with different degrees of readiness. Cast iron is often protected by its *casting skin*. Impurities present in steel often favor corrosion by causing electric couples to be established.

A. Ferrous Compounds

Ferrous compounds, which may be prepared by dissolving metallic iron, ferrous oxide, ferrous hydroxide, ferrous carbonate, or ferrous sulfide, etc., in acids, are usually greenish in the crystallized state, but in the anhydrous condition they are white, yellow, or bluish; in concentrated solution they are green; in dilute solutions almost colorless. Ferrous compounds exhibit a strong tendency to change over into ferric salts: they are strong reducing agents.

Reactions in the Wet Way

1. **Alkali Carbonates** precipitate the white carbonate,

$$FeCl_2 + Na_2CO_3 \rightarrow 2\,NaCl + \mathbf{FeCO_3}$$

which in contact with the air becomes green, then brown:

$$4\,\mathbf{FeCO_3} + 6\,H_2O + O_2 \rightarrow 4\,CO_2\uparrow + 4\,\mathbf{Fe(OH)_3}$$

being converted into ferric hydroxide with loss of carbonic anhydride.

Ferrous carbonate, like calcium carbonate (cf. p. 261), is soluble in carbonic acid, forming ferrous bicarbonate:

$$\mathbf{FeCO_3} + H_2CO_3 \rightarrow Fe(HCO_3)_2$$

a compound which is found in many natural waters, but which, like the normal carbonate, is decomposed by atmospheric oxygen with separation of ferric hydroxide:

$$4\,Fe(HCO_3)_2 + 2\,H_2O + O_2 \rightarrow 8\,CO_2\uparrow + 4\,\mathbf{Fe(OH)_3}$$

Consequently a mineral water which contains ferrous bicarbonate, if allowed to stand in contact with the air, will become turbid, owing to the deposition of ferric hydroxide. To prevent this, the bottle

must be filled with water and tightly corked, so that no trace of air can get in. Ferric hydroxide is insoluble in carbonic acid.

2. **Alkali Hydroxides,** if air is excluded, produce complete precipitation of white ferrous hydroxide,

$$Fe^{++} + 2\,OH^- \rightarrow \mathbf{Fe(OH)_2}$$

which is oxidized by the air into ferric hydroxide. The oxidation takes place immediately upon the addition of sodium peroxide:

$$2\,Fe^{++} + Na_2O_2 + 2\,OH^- + 2\,H_2O \rightarrow 2\,\mathbf{Fe(OH)_3} + 2\,Na^+$$

3. **Ammonia** produces in neutral solutions an incomplete precipitation of ferrous hydroxide which is white when precipitated out of contact with air:

$$FeCl_2 + 2\,NH_3 + 2\,H_2O \rightleftarrows \mathbf{Fe(OH)_2} + 2\,NH_4Cl$$

Ferrous salts in this respect are similar to those of magnesium (cf. p. 271). In the presence of ammonium chloride the reaction takes place in the direction from right to left; ammonia, therefore, causes no precipitation with ferrous salts out of contact with the air, provided sufficient ammonium chloride is present. On exposure to the air, however, a turbidity is soon formed, green at first, then almost black, and finally becoming brown. The small amount of ferrous hydroxide contained in the solution is oxidized by the air, forming at first black ferrous-ferric hydroxide and finally brown ferric hydroxide.

4. **Ammonium Sulfide** precipitates iron completely as black ferrous sulfide:

$$FeCl_2 + (NH_4)_2S \rightarrow 2\,NH_4Cl + \mathbf{FeS}$$

which is readily soluble in acids with evolution of hydrogen sulfide. In moist air it turns slightly brown, a part of the sulfur separates out, and a basic ferric sulfate is formed.

5. **Ammonium Thioacetate,*** CH_3COSNH_4, gives no reaction in an acid solution of a ferrous salt, but ferrous sulfide is precipitated in an alkaline solution:

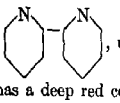
$$CH_3COS^- + Fe^{++} + 2\,OH^- \rightarrow C_2H_3O_2^- + \mathbf{FeS} + H_2O$$

Sodium thiosulfate, however, does not cause precipitation.

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* Acetic acid is $HC_2H_3O_2$ or, as the organic chemist prefers, $CH_3CO \cdot OH$. Thioacetic acid has the same formula except that the last oxygen is replaced by sulfur. It is made by the action of phosphoric pentasulfide upon glacial acetic acid. The substance has an unpleasant odor and is fairly expensive. Schiff and Tarugi (*Z. anal. Chem.*, **34**, 456) have recommended the use of a faintly ammoniacal solution of the ammonium salt instead of hydrogen sulfide. It is a very effective precipitant of sulfides. Sodium thiosulfate will give sulfide precipitates with many cations but its sulfur atom with the negative valence of two is less accessible than in thioacetic acid.

6. **Dimethylglyoxime**, $(CH_3)_2C_2(NOH)_2$, added to a ferrous solution containing tartaric acid, gives, upon the addition of ammonia, a deep reddish coloration. As the ferrous iron oxidizes, the color fades. This reaction is sensitive.

7. **α-α′-Dipyridyl**, $C_{10}H_8N_2$ or  , unites with ferrous ions to form a complex bivalent cation which has a deep red color. The reagent, a 2 per cent solution of the base in dilute hydrochloric acid or in alcohol, does not react with ferric ions. The test is so sensitive that 0.03 γ of iron can be detected in a single drop of solution on a spot plate. The dipyridyl combines with Fe^{++} to form a complex cation just as NH_3 unites with Cu^{++}; the union of the entire neutral molecule does not change the valence of the original cation. Dipyridyl forms addition compounds with other metal cations in acid solutions but the products do not have deep colors that interfere with the test for iron.

8. **Hydrogen Sulfide** produces no precipitation in acid solutions of ferrous salts; in dilute neutral solutions a small amount of black ferrous sulfide is precipitated; but if the solution contains *considerable alkali acetate*, hydrogen sulfide precipitates more of the iron as ferrous sulfide (but not all of it), in spite of the fact that ferrous sulfide is readily soluble in acetic acid. This interesting fact is an instructive illustration of the law of chemical mass action.

The table on page 22 states that 3.4×10^{-8} g of ferrous sulfide dissolves in a liter of water. This small quantity exists in solution almost entirely as Fe^{++} and S^{--} ions. $FeS \rightleftarrows Fe^{++} + S^{--}$. When acetic acid, which is a much stronger acid than hydrogen sulfide (cf. p. 11), is added to the solution, equilibrium has to be established between its hydrogen ions and the dissolved sulfide ions, $2\,H^+ + S^{--} \rightleftarrows H_2S$, and, as a result of the formation of non-ionized hydrogen sulfide, the solution no longer contains enough sulfur ions to reach the value of the solubility product of FeS; to restore the equilibrium between FeS and its ions, more of the solid must dissolve. If, moreover, the solution is boiled, the hydrogen sulfide escapes as a gas as soon as it is formed. Consequently it is impossible to arrive at a state of equilibrium until all the ferrous sulfide has dissolved. The solution is accomplished by means of hydrogen ions:

$$FeS + 2\,H^+ \rightleftarrows Fe^{++} + H_2S\uparrow$$

On the other hand, if the ionization of the acetic acid is repressed by adding an alkali acetate to the solution (cf. p. 49), and the concentration of the hydrogen sulfide is made as large as possible by keeping the solution saturated with the gas, the reaction will take place in the reverse direction and some of the iron will be precipitated as ferrous sulfide.

9. **α-Nitroso-β-naphthol**, $C_{10}H_6(NO)OH$, gives a green coloration with dilute solutions of ferrous salts and, on standing, a flocculent precipitate of ferrous nitroso-β-naphthol is formed. Hydrogen ions, even the small quantity formed by the hydrolysis of a ferric salt, prevent this reaction. Sodium acetate must be added in the latter case. The precipitate oxidizes easily to the corresponding ferric compound.

10. **Potassium Cyanide** precipitates yellowish brown ferrous cyanide,

$$Fe^{++} + 2\,CN^- \rightarrow Fe(CN)_2$$

which is soluble in excess of the reagent, forming potassium ferrocyanide:

$$Fe(CN)_2 + 4\ CN^- \rightarrow [Fe(CN)_6]^{----}$$

The complex ferrocyanide anion is in equilibrium, to be sure, with simple ferrous cations, but the quantity of the latter present in the aqueous solution of a ferrocyanide is so small that none of the above reactions characteristic of ferrous ions can be obtained with it. Many similar complex cyanide anions are known; thus, the cyanides of silver, nickel, iron (ferrous and ferric), and cobalt all dissolve in potassium cyanide, forming the following complex ions: $[Ag(CN)_2]^-$, $[Ni(CN)_4]^{--}$, $[Fe(CN)_6]^{---}$, $[Fe(CN)_6]^{--}$, $[Co(CN)_6]^{---}$. The acids are:

$$H[Ag(CN)_2],\ H_2[Ni(CN)_4],\ H_3[Fe(CN)_6],\ H_4[Fe(CN)_6],\ H_3[Co(CN)_6]$$

It is possible, as a matter of fact, to isolate the last three acids, though the two former have never been prepared; they immediately break down into metallic cyanide and hydrocyanic acid, just as carbonic acid is decomposed into water and carbon dioxide.

With iron, therefore, there are two series of complex cyanogen compounds, the ferrocyanides and the ferricyanides. The ferrocyanide derivatives contain the quadrivalent ferrocyanide anion, and the ferricyanides contain the trivalent ferricyanide anion.

Potassium ferrocyanide, $K_4[Fe(CN)_6]$, is often called *yellow prussiate of potash*, and potassium ferricyanide, $K_3[Fe(CN)_6]$, is called *red prussiate of potash*. The solubility of the alkali and alkaline-earth salts, and the insolubility and color of the salts of the heavy metals (especially with both ferric and ferrous iron), are very characteristic of ferro- and ferricyanides.

$$Fe(CN)_2 + 4\ CN^- \rightarrow [Fe(CN)_6]^{----}$$

11. Potassium Ferricyanide, $K_3[Fe(CN)_6]$, added to solutions of ferrous salts produces a dark blue precipitate (Turnbull's blue) consisting of ferrous ferricyanide mixed with potassium ferric ferrocyanide:

$$2\ K_3[Fe(CN)_6] + 3\ FeCl_2 \rightarrow 6\ KCl + Fe_3[Fe(CN)_6]_2$$

and

$$K_3[Fe(CN)_6] + FeCl_2 \rightarrow KFe^{+++}[Fe(CN)_6]^{---} + 2\ KCl$$

In other words, the ferricyanide acts both as a precipitant and as an oxidizing agent* and a blue color results whenever iron is present in the cation in a state of oxidation different from that of the iron present in the complex anion. The ferricyanide ion is a strong oxidizing agent and in alkaline solution readily oxidizes ferrous hydroxide to ferric hydroxide. Turnbull's blue is not very soluble in acid solutions, but is decomposed by treatment with caustic alkali, all of the complex anion being in the form of ferrocyanide:

$$Fe_3^{++}[Fe(CN)_6]_2^{---} + 8\ KOH \rightarrow 2\ K_4[Fe(CN)_6] + 2\ Fe(OH)_3 + Fe(OH)_2$$

$$K^+Fe^{+++}[Fe(CN)_6]^{---} + 3\ KOH \rightarrow K_4[Fe(CN)_6] + Fe(OH)_3$$

12. Potassium Ferrocyanide, $K_4[Fe(CN)_6]$, produces in solutions of ferrous salts, *with complete exclusion of air, a white* precipitate of *potassium ferrous ferrocyanide* or of *ferrous ferrocyanide*, depending

* Cf. Erich Muller, *J. prakt. Chem.*, **84**, 353 (1911).

upon whether one or two molecules of ferrous salt react with one molecule of potassium ferrocyanide:

$$K_4[Fe(CN)_6] + FeSO_4 \rightarrow K_2SO_4 + \mathbf{K_2Fe[Fe(CN)_6]}$$
$$K_4[Fe(CN)_6] + 2\,FeSO_4 \rightarrow 2\,K_2SO_4 + \mathbf{Fe_2[Fe(CN)_6]}$$

Although both the above salts are white, a *light blue* color is almost always obtained, because the precipitate is immediately oxidized somewhat by the air, forming the *ferric* salt of hydroferrocyanic acid (Prussian blue):

$$6\,Fe_2[Fe(CN)_6] + 6\,H_2O + 3\,O_2 \rightarrow \underset{\text{Prussian blue}}{\mathbf{2\,Fe_4[Fe(CN)_6]_3}} + 4\,\mathbf{Fe(OH)_3}$$

13. **Potassium Thiocyanate** gives no reaction with ferrous salts (note difference from ferric salts).

As has been stated, ferrous salts are oxidized by the air to ferric salts; thus ferrous sulfate is gradually changed into brown, basic ferric sulfate,

$$4\,FeSO_4 + O_2 \rightarrow 2\,[Fe_2O \cdot (SO_4)_2]$$

which is insoluble in water. Consequently it often happens that ferrous sulfate will not dissolve in water to a clear solution, but gives a brown, turbid solution, becoming clear on the addition of acid, the basic ferric salt being changed to a soluble neutral salt:

$$Fe_2O \cdot (SO_4)_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$$

Such a solution, which then contains ferric ions, reacts with potassium thiocyanate (cf. p. 215). To free the solution from ferric salt, it may be boiled with metallic iron, out of contact with air, whereby the ferric salt is changed into ferrous salt:

$$Fe_2(SO_4)_3 + Fe \rightarrow 3\,FeSO_4$$

By means of strong oxidizing agents, ferrous salts can be quickly and completely changed into ferric salts, as was shown in the Introduction (cf. pp. 31–35).

DETECTION OF FERROUS OXIDE IN THE PRESENCE OF METALLIC IRON

Treat the mixture with a large excess of a neutral solution of mercuric chloride and heat on the water-bath; the metallic iron goes into solution as ferrous chloride:

$$2\,HgCl_2 + Fe \rightarrow FeCl_2 + Hg_2Cl_2$$

Filter off the residue and test the filtrate with potassium ferricyanide; a precipitate of Turnbull's blue shows that metallic iron was originally present.

Wash the residue with cold water, until all the ferrous chloride has been dissolved, and then treat it with dilute hydrochloric acid. If hydrogen is given off, some metallic iron is still present; the experiment must be repeated and the mixture given a longer treatment with $HgCl_2$ solution. If the solution now gives a precipitate of Turnbull's blue with potassium ferricyanide, ferrous oxide was present.

B. Ferric Compounds

Ferric oxide, Fe_2O_3, is reddish brown, becomes grayish black on strong ignition but on being pulverized appears red again.

Ferric salts are usually yellow or brown, but ferric ammonium alum is pale violet.

Ferric salts are yellowish brown in aqueous solution, and the solution reacts acid (hydrolysis). Dilution and warming favor the hydrolysis, so that all strongly diluted ferric salts deposit basic salts on being boiled:

$$Fe_2(SO_4)_3 + H_2O \rightleftarrows Fe_2(SO_4)_2O + H_2SO_4$$

With ferric salts of the weaker acids, often all the iron is precipitated as a basic salt; thus the acetate, on being boiled in a dilute solution, reacts as follows:

$$Fe(C_2H_3O_2)_3 + 2\,H_2O \rightleftarrows Fe(OH)_2(C_2H_3O_2) + 2\,HC_2H_3O_2$$

By the addition of acid all basic salts may be changed back into neutral salts.

Reactions in the Wet Way

1. **Alkali Hydroxides** and **Ammonia** precipitate brown, gelatinous ferric hydroxide:

$$Fe^{+++} + 3\,OH^- \rightarrow \mathbf{Fe(OH)_3}$$

The solubility product of ferric hydroxide is so small (cf. p. 22) that it is precipitated completely even in the presence of ammonium salts; it is readily soluble in acids. On ignition it loses water and is changed to oxide, which is very difficultly soluble in dilute acids. It is best brought into solution by long-continued heating below the boiling point with concentrated hydrochloric acid.

In spite of the slight solubility of ferric hydroxide, it is not formed in the presence of many organic substances with which ferric ions unite to form complexes. (See below.)

2. **Alkali Acetates** produce in cold, neutral solutions a dark brown coloration, and on boiling the dilute solution all the iron separates as basic acetate:

$$Fe^{+++} + 3\,C_2H_3O_2^- \rightarrow Fe(C_2H_3O_2)_3 \text{ (in the cold)}$$

$$Fe(C_2H_3O_2)_3 + 2\,H_2O \rightarrow 2\,HC_2H_3O_2 + \mathbf{Fe(OH)_2C_2H_3O_2} \text{ (on boiling)}$$

The presence of organic hydroxy-acids (tartaric, malic, citric, etc.) and of polyatomic alcohols (glycerol, erythritol, mannitol, sugars, etc.) prevent all the above-mentioned reactions, because complex salts are formed in which the iron is present in the form of a complex anion (cf. aluminum, pp. 190 and 193). Tannin, however, yields a violet-black precipitate in the tartrate solution containing ammonium acetate.

3. **Alloxantine,** $C_8H_6O_8N_4$, gives a blue color with ferric ions and dilute sodium hydroxide.*

4. **Ammonium Sulfide** added to a solution of a ferric salt gives a precipitate of ferric sulfide, Fe_2S_3,

$$2\,Fe^{+++} + 3\,S^{--} \rightarrow \mathbf{Fe_2S_3}$$

* Denigés, *Compt. rend.*, **180**, 519 (1925).

which is soluble in cold, dilute hydrochloric acid, forming ferrous chloride and sulfur:

$$Fe_2S_3 + 4\,H^+ \rightarrow 2\,Fe^{++} + 2\,H_2S\uparrow + S$$

The fact that Fe_2S_3 is precipitated, and not FeS as formerly believed, was proved by H. N. Stokes* who decomposed it out of contact with air by zinc ammonium oxide and obtained white ZnS and red $Fe(OH)_3$. L. Gedel† has also shown that hydrogen sulfide passed into a solution of ferric chloride made alkaline with ammonia gives Fe_2S_3. If, however, the solution is acid, hydrogen sulfide or ammonium sulfide reduces the ion before any precipitate is formed.

5. **Ammonium Thioacetate,** $NH_4C_2H_3OS$, reduces ferric salts in acid solutions and precipitates ferrous sulfide if alkali is present:

$$2\,Fe^{+++} + C_2H_3OS^- + H_2O \rightarrow 2\,Fe^{++} + HC_2H_3O_2 + H^+ + S$$

$$2\,Fe^{+++} + 3\,C_2H_3OS^- + 6\,OH^- \rightarrow 2\,FeS + 3\,C_2H_3O_2^- + 3\,H_2O + S$$

6. **Cobalt Chloride** dissolved in concentrated hydrochloric acid gives a deep blue solution. If a little of this blue liquid is added to a solution containing a small quantity of ferric ions, a green color is obtained. Venable has recommended this reaction as a test for ferric ions in acids or for detecting ferric ions in the presence of ferrous ions.

7. **Cupferron,** the ammonium salt of phenylnitrosohydroxylamine, $C_6H_5NO \cdot NONH_4$, precipitates red $(C_6H_5NO \cdot NO)_3Fe$, which is soluble in ether, insoluble in acids, and converted into $Fe(OH)_3$ by treatment with ammonia.

8. **Ether** when shaken with a solution of ferric chloride in 6 *N* hydrochloric acid dissolves most of the ferric chloride. By separating the the ether with the aid of a separatory funnel, keeping the aqueous solution 6 *N* in HCl and repeating the operation, nearly all the iron can be removed from the aqueous solution. (Cf. p. 14.)

9. **Hydrogen Sulfide** in acid solutions reduces ferric salts to ferrous salts, with separation of sulfur:

$$2\,Fe^{+++} + H_2S \rightarrow 2\,Fe^{++} + 2\,H^+ + S$$

Besides hydrogen sulfide, many other substances (metals, stannous chloride, sulfurous acid, hydriodic acid, etc.) will reduce ferric salts, as was shown on pages 37–39.

10. **α-Nitroso-β-naphthol,** $C_{10}H_6(NO)OH$, gives a voluminous, brownish black precipitate of ferric nitroso-β-naphthol, $(C_{10}H_6NO \cdot O)_3Fe$, in neutral or slightly acid solutions.

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* *J. Am. Chem. Soc.*, **29** (1907), 304.

† *Ueber Schwefeleisen*, Karlsruhe (1905).

11. **Potassium Ferricyanide,** $K_3[Fe(CN)_6]$, produces no precipitation in solutions of ferric salts, only a brown coloration (differing from ferrous salts):

$$[Fe(CN)_6]^{---} + Fe^{+++} \rightleftarrows 2\ Fe(CN)_3$$

12. **Potassium Ferrocyanide,** $K_4[Fe(CN)_6]$, produces in neutral or acid solutions of ferric salts an intense blue precipitate of Prussian blue; 0.1 γ of Fe^{+++} will give the test in 1 drop of solution:

$$3\ [Fe(CN)_6]^{----} + 4\ Fe^{+++} \rightarrow \mathbf{Fe_4[Fe(CN)_6]_3}$$

Prussian blue, the ferric salt of ferrocyanic acid, is insoluble in water, but soluble in oxalic acid and in an excess of potassium ferrocyanide; the solution thus obtained is a deep blue and is used as bluing and a blue ink. The blue solution obtained with a ferric salt and an excess of potassium ferrocyanide contains colloidal $KFe[Fe(CN)_6] \cdot H_2O$, which can be *salted out* by the addition of a considerable quantity of electrolyte such as alkali chloride, sulfate or nitrate. Prussian blue is also soluble in concentrated hydrochloric acid, but is precipitated again on dilution. As the ferric salt of ferrocyanic acid it behaves like other ferric salts to the hydroxides of the alkalies, ferric hydroxide and the alkali salt of hydroferrocyanic acid being formed:

$$\mathbf{Fe_4[Fe(CN)_6]_3} + 12\ OH^- \rightarrow 4\ \mathbf{Fe(OH)_3} + 3\ [Fe(CN)_6]^{----}$$

13. **Potassium Thiocyanate,** KCNS, produces in solutions of ferric salts a blood-red coloration:

$$Fe^{+++} + 3\ CNS^- \rightleftarrows Fe(CNS)_3$$

This action is reversible; the red color of the slightly ionized ferric thiocyanate being most intense when an excess of ferric salt, or of potassium thiocyanate, is present. Some say that the red color is that of $[(Fe(CNS)]^{++}$.

If the solution is shaken with ether, the $Fe(CNS)_3$ goes into the ether. Ferric thiocyanate combines readily with potassium thiocyanate, forming complex potassium ferrithiocyanate:

$$Fe(CNS)_3 + 3\ KCNS \rightarrow K_3[Fe(CNS)_6]\ *$$

Analogous to potassium ferricyanide, $K_3[Fe(CN)_6]$.

The complex salt is insoluble in ether, the $Fe(CNS)_3$ only being soluble therein, so that the red color is due to the formation of the ferric thiocyanate and not to the complex salt.

This reaction is extremely sensitive, but not always reliable. In ferric solutions which are more or less red by the presence of ferric-acetate-complex ions, the red color of ferric thiocyanate can be seen only when considerable hydrochloric acid is added. Similarly if the solution contains oxalic, tartaric, citric, malic, iodic, phosphoric, arsenic or hydrofluoric acid, the red color is not obtained except when nitric acid is present. The test must then be made in the cold solution because hot nitric acid decomposes the thiocyanate ion and, at the same time, the nitrite ion on its part gives a red coloration with thiocyanate; this nitrite color disappears, however, upon heating with a little alcohol, which does not affect ferric thiocyanate.

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* $K_3[Fe(CNS)_6] \cdot 4\ H_2O$. Cf. Rosenheim, *Z. anorg. Chem.*, **27**, 208 (1901).

The sensitiveness of the reaction can be increased somewhat by adding an excess of freshly prepared potassium thiocyanate solution and shaking with ether. In the presence of mercuric chloride the red color disappears entirely; the mercuric chloride reacts with the ferric thiocyanate, forming a colorless, soluble mercuric double salt, which is ionized even less than ferric thiocyanate:

$$2\,Fe(CNS)_3 + 6\,HgCl_2 \rightarrow 2\,FeCl_3 + 3\,[Hg(CNS)_2 \cdot HgCl_2]$$

14. **Sodium Carbonate** produces a brown precipitate of basic carbonate, which at the boiling temperature is completely decomposed hydrolytically into hydroxide and carbon dioxide:

$$2\,FeCl_3 + 3\,Na_2CO_3 + 3\,H_2O \rightarrow 2\,Fe(OH)_3 + 6\,NaCl + 3\,CO_2\uparrow$$

15. **Sodium Phosphate** precipitates yellowish white ferric phosphate:

$$Fe^{+++} + 2\,HPO_4^{--} \rightarrow H_2PO_4^{-} + FePO_4$$

Ferric phosphate is insoluble in acetic acid, but readily soluble in mineral acids. The precipitation of iron with sodium hydrogen phosphate is complete only when a considerable excess of the precipitant is employed, or when sodium acetate is added:

$$Fe^{+++} + HPO_4^{--} + C_2H_3O_2^{-} \rightarrow HC_2H_3O_2 + FePO_4$$

In this last case all the iron and all the phosphoric acid are precipitated. The reaction is often used to precipitate phosphoric acid quantitatively. An excess of the disodium phosphate will also cause complete precipitation of iron as phosphate, if the phosphate solution is previously exactly neutralized with ammonia:

$$HPO_4^{--} + NH_4 \rightarrow NH_4^{+} + PO_4^{---}$$

and

$$PO_4^{---} + Fe^{+++} \rightarrow FePO_4$$

If, however, an excess of sodium phosphate and ammonia is added to the iron sclution, the precipitation of iron is incomplete, because the ferric phosphate dissolves in the excess of sodium phosphate, in the presence of ammonia (or ammonium carbonate), with a brown color and formation of a complex salt.

Ferric phosphate is transformed by ammonia into a brown basic phosphate, and by potassium hydroxide almost completely into ferric hydroxide and potassium phosphate; by *fusion* with caustic alkali or alkali carbonate it is completely decomposed.

If alkaline earth ions are present, an excess of ammonia completely changes ferric phosphate to ferric hydroxide and alkaline earth phosphate is precipitated.

16. **Sodium Thiosulfate,** $Na_2S_2O_3$, colors neutral ferric solutions a violet red, but the color disappears quickly and the solution then contains *ferrous* salt and *sodium tetrathionate:*

$$2\,S_2O_3^{--} + 2\,Fe^{+++} \rightarrow 2\,Fe^{++} + S_4O_6^{--}$$

The composition of the violet-red substance which is first formed is unknown; perhaps it is ferric *thiosulfate.*

17. **Zinc Oxide, Mercuric Oxide, and Barium Carbonate** also precipitate ferric iron as hydroxide:

$$2\ FeCl_3 + 3\ ZnO + 3\ H_2O \rightarrow 3\ ZnCl_2 + 2\ Fe(OH)_3$$

This reaction is frequently used in quantitative analysis, *e.g.*, to separate Fe^{+++} from Mn^{++}.

DETECTION OF IRON IN COMPLEX SALTS

As we have seen, there exist a number of iron compounds which contain the metal as a complex ion, so that it cannot be detected by the ordinary reagents. The complex organic hydroxy-compounds, as well as the ferro- and ferricyanides, belong to this class of compounds.

If it is a question of detecting the presence of iron in such a compound, a different method should be used in the case of an organic hydroxy-compound from that in the case of a ferro- or ferricyanide.

If organic substances are present, the iron is precipitated as sulfide by means of ammonium sulfide; or the organic matter is first removed by ignition, whereby metallic iron, oxides of iron and some carbon are obtained.

If we have a ferro- or ferricyanide, the iron cannot be precipitated even by means of ammonium sulfide; the compound must be completely destroyed before it will be possible to detect the presence of iron by any of the ordinary methods.

This may be accomplished (*a*) by ignition, (*b*) by fusion with potassium carbonate or sodium carbonate, or (*c*) by heating strongly with concentrated sulfuric acid.

(*a*) *Decomposition by Ignition.* — The ferrocyanides and ferricyanides are all decomposed by ignition, but the products of the decomposition vary according to the conditions. The alkali salts yield alkali cyanide, iron carbide, and nitrogen, but some hydrocyanic acid, carbon dioxide, ammonia, and cyanogen are also obtained. The reaction is reversible, and it is possible to utilize the reversed reaction for the fixation of atmospheric nitrogen; iron, carbon, alkali carbonate, and nitrogen are heated together and some alkali ferrocyanide is obtained.

After the ignition of the complex cyanide, extract the residue with water, whereby any alkali cyanide is removed. Filter and treat the residue with dilute hydrochloric acid; iron and iron carbide dissolve as ferrous chloride, hydrocarbons are evolved, and some carbon remains undissolved.

(*b*) *Decomposition by Means of Fusion with Potassium Carbonate.* — Mix the substance with an equal amount of the carbonate and heat in a porcelain crucible until a quiet fusion is obtained. By this means a mixture of potassium cyanide and potassium cyanate (both soluble in water) is formed in the presence of metallic iron:

$$K_4[Fe(CN)_6] + K_2CO_3 \rightarrow 5\ KCN + KCNO + CO_2\uparrow + Fe$$

Extract the melt with water, filter, and dissolve the iron in hydrochloric acid.

(*c*) *Decomposition by Heating with Concentrated Sulfuric Acid.* — By heating with concentrated sulfuric acid all complex cyanide compounds may be decomposed. By this means the metal present is changed into sulfate, the nitrogen of the cyanide into ammonium sulfate, while the carbon of the cyanide escapes as carbon monoxide:

$$K_4[Fe(CN)_6] + 6\ H_2SO_4 + 6\ H_2O \rightarrow 2\ K_2SO_4 + FeSO_4 + 3\ (NH_4)_2SO_4 + 6\ CO\uparrow$$

$$2\ K_3[Fe(CN)_6] + 12\ H_2SO_4 + 12\ H_2O \rightarrow 3\ K_2SO_4 + Fe_2(SO_4)_3 + 6\ (NH_4)_2SO_4 + 12\ CO\uparrow$$

The treatment with concentrated sulfuric acid is best accomplished in a porce-

lain crucible placed in an inclined position over the flame, and the flame directed against the upper part of the crucible. Continue heating until fumes of sulfuric acid cease to come off. Treat the residue, which consists of an alkali sulfate and anhydrous ferrous or ferric sulfate, with a little concentrated sulfuric acid, heat gently, and add water little by little. In this way the sulfate is readily brought into solution.

Reactions in the Dry Way

The borax and the sodium metaphosphate beads, containing a small amount of an iron salt, are yellow while hot and colorless when cold after being heated in the oxidizing flame, and pale green after being heated in the reducing flame. When strongly saturated, however, the bead obtained with the oxidizing flame is brown while hot, yellow when cold; and after heating in the reducing flame it becomes bottle-green.

Heated on charcoal with soda before the blowpipe, all iron compounds leave a gray particle of metallic iron, which is usually difficult to see, but it can be separated from the charcoal by means of the magnet. The reduction on the charcoal stick, as described on page 75, is a much more delicate test.

MANGANESE, Mn. At. Wt. 54.93, At. No. 25

Density 7.2. M. P. 1264° ± 10°. B. P. 1900°

Occurrence. — The most important manganese minerals are pyrolusite, MnO_2, orthorhombic; polianite, also MnO_2, tetragonal, isomorphous with rutile and tinstone; braunite, Mn_2O_3, tetragonal; manganite, $HMnO_2$, orthorhombic, isomorphous with goethite and diaspore; hausmannite, Mn_3O_4, tetragonal; and rhodochrosite, $MnCO_3$. Manganese is a constant companion of iron, so that we find it in varying amounts in almost all iron ores.

Properties. — Manganese, although it derives its name from the Latin *magnes* = magnet, is a brittle, non-magnetic metal which, like iron, can be hardened by alloying with carbon. It is easily oxidized and decomposes water, with liberation of hydrogen, at temperatures but slightly above room temperature. The metal is dissolved by dilute acids, even acetic acid. It is used largely as ferromanganese in the manufacture of steel. Small quantities of manganese accomplish the deoxidation of steel, and large quantities produce a very tough "self-hardening" steel. Manganese dioxide is used in dry cells, as a drier for paints and varnishes, and for coloring glass and ceramic ware.

Oxides, Hydroxides, and Salts. — Five oxides of manganese are known, and salts exist corresponding to a sixth (MnO_3). Manganous oxide, MnO, is formed by heating $Mn(OH)_2$, $MnCO_3$, or MnC_2O_4 out of contact with air, or by heating another oxide of manganese in hydrogen. It is a gray or greenish gray powder which oxidizes in the air to Mn_3O_4. Manganous hydroxide, $Mn(OH)_2$ is formed by the addition of alkali hydroxide to a solution of manganous salt. It oxidizes readily to *form $Mn(OH)_3$ or $MnO(OH)$. Manganic oxide, Mn_2O_3, can be made by heating MnO_2* for a long time at 700°. The hydroxide forms unstable manganic salts with acids, but, as a rule, it behaves as if it were composed of one atom of bivalent manganese and one of quadrivalent manganese which justifies the name manganous metaman-

ganite. The oxide Mn_3O_4 occurs in nature as the mineral hausmannite and can be called trimanganese tetroxide, but its behavior toward dilute nitric or sulfuric acid suggests that it is really manganous orthomanganite. Manganese dioxide, MnO_2, is found in nature as pyrolusite and can be formed by heating manganous nitrate to 200° in the air, or by boiling a manganous salt with concentrated nitric acid and potassium chlorate. It can be regarded as the anhydride of manganous acid, H_2MnO_3. The oxide MnO_3 has never been isolated. It is the anhydride of manganic acid, H_2MnO_4, which exists only in the form of salts. The oxide Mn_2O_7 is the anhydride of permanganic acid; it is an oily reddish brown liquid which is so unstable that it explodes violently on gentle heating.

By treating any oxide of manganese, except MnO, with cold, dilute hydrochloric acid, a dark greenish brown solution is obtained, which on being heated evolves chlorine and becomes colorless. The solution then contains a bivalent manganese salt — a derivative of MnO. Manganous oxide dissolves in acid without evolution of chlorine.

$$MnO + 2\,HCl \rightarrow H_2O + MnCl_2$$
$$Mn_2O_3 + 6\,HCl \rightarrow 3\,H_2O + 2\,MnCl_2 + Cl_2\uparrow$$
$$Mn_3O_4 + 8\,HCl \rightarrow 4\,H_2O + 3\,MnCl_2 + Cl_2\uparrow$$
$$MnO_2 + 4\,HCl \rightarrow 2\,H_2O + MnCl_2 + Cl_2\uparrow$$
$$Mn_2O_7 + 14\,HCl \rightarrow 7\,H_2O + 2\,MnCl_2 + 5\,Cl_2\uparrow$$

All manganese oxides dissolve on warming with concentrated sulfuric acid, forming manganous sulfate, accompanied (with the exception of MnO) by evolution of oxygen:

$$MnO + H_2SO_4 \rightarrow H_2O + MnSO_4$$
$$2\,Mn_2O_3 + 4\,H_2SO_4 \rightarrow 4\,H_2O + 4\,MnSO_4 + O_2\uparrow$$
$$2\,Mn_3O_4 + 6\,H_2SO_4 \rightarrow 6\,H_2O + 6\,MnSO_4 + O_2\uparrow$$
$$2\,MnO_2 + 2\,H_2SO_4 \rightarrow 2\,H_2O + 2\,MnSO_4 + O_2\uparrow$$

The behavior of the higher oxides, MnO_2, Mn_2O_3, and Mn_3O_4, with boiling dilute nitric or sulfuric acid is interesting: MnO_2 is not attacked at all by these dilute acids; Mn_2O_3 gives up half of its manganese to the acid, the other half remaining undissolved as brown hydrated manganese dioxide, H_2MnO_3; two-thirds of Mn_3O_4 is dissolved by these acids, brown hydrated manganese dioxide being left behind, as before. This H_2MnO_3 separates out just as metasilicic acid is deposited from a silicate on the addition of a strong acid:

$$CaSiO_3 + 2\,H^+ \rightarrow H_2SiO_3 + Ca^{++}$$

In fact, hydrated manganese dioxide behaves in most reactions exactly like an acid; the oxides Mn_2O_3 and Mn_3O_4 behave like manganous salts of this acid and are to be regarded as manganites.

Mn_2O_3, therefore, is to be regarded as manganous manganite, $Mn\langle{}^{O}_{O}\rangle MnO$, of analogous composition to manganous carbonate, $MnCO_3$, and manganous metasilicate, $MnSiO_3$. According to this conception, electrolytic dissociation should give rise to Mn^{++} cations and MnO_3^{--} anions; it is easy to understand, therefore, why Mn_2O_3 gives up half of its manganese on treatment with dilute nitric acid, with the separation of manganous acid:

$$MnMnO_3 + 2\,HNO_3 \rightleftarrows Mn(NO_3)_2 + H_2MnO_3$$

Mn_3O_4, which gives up two-thirds of its manganese, may be considered to be the manganous salt of orthomanganous acid, H_4MnO_4.

On treating Mn_2MnO_4 with nitric acid, the ortho-acid first separates out; it loses water, and goes over into metamanganous acid:

$$Mn_2MnO_4 + 4\,HNO_3 \rightarrow 2\,Mn(NO_3)_2 + H_4MnO_4$$
$$H_4MnO_4 \rightarrow H_2O + H_2MnO_3$$

MnO_2 stands in the same relation to H_2MnO_3 as CO_2 to H_2CO_3, as SiO_2 to H_2SiO_3, and as SnO_2 to H_2SnO_3; MnO_2, therefore, behaves like an acid anhydride. Like SnO_2 (which see), manganese dioxide behaves partly as an acid anhydride and partly as the anhydride of a base. It probably forms the chloride $MnCl_4$, for if MnO_2 is treated with cold concentrated hydrochloric acid it dissolves with a brownish green color, forming manganese tetrachloride, soluble in ether with a green color. If, therefore, the aqueous solution of $MnCl_4$ is shaken with ether, the upper layer is colored green.

$Mn(SO_4)_2$ and $Mn_2(SO_4)_3$ are also known. These salts are hydrolyzed readily, forming H_2MnO_3 and $MnMnO_3$:

$$Mn(SO_4)_2 + 3\,H_2O \rightleftarrows H_2MnO_3 + 2\,H_2SO_4$$
$$Mn_2(SO_4)_3 + 3\,H_2O \rightleftarrows Mn_2O_3 + 3\,H_2SO_4$$

Not only manganous manganites, but quite a number of other manganites are known. Some of these play a very important part in analytical chemistry — for example, zinc and calcium bimanganites $ZnH_2(MnO_3)_2$, $CaH_2(MnO_3)_2$, which are analogous to calcium bicarbonate, $CaH_2(CO_3)_2$. Zinc bimanganite is formed in the volumetric determination of manganese (see Vol. II). Calcium bimanganite is of importance technically; thus the recovery of manganese, by the Weldon process in the manufacture of chlorine, depends upon the formation of calcium bimanganite.

Manganous oxide, MnO, is the only oxide of manganese which always acts as the anhydride of a base. By dissolving this oxide in acids, manganous salts are always obtained, in which the manganese is bivalent. The oxide MnO_3 has never been isolated, but salts (R_2MnO_4, see p. 227) are known which are derived from it. Mn_2O_7 is a distinct acid anhydride, from which the permanganates ($RMnO_4$) are derived.

In the study of the reactions of manganese, the manganous compounds will be discussed first, then the manganates and permanganates.

A. Manganous Compounds

The manganous compounds are pink both in the crystalline state and in aqueous solution; but in the anhydrous state they are colorless with the exception of the sulfide.

Reactions in the Wet Way

1. **Alkali Hydroxides** precipitate white manganous hydroxide,

$$Mn^{++} + 2\,OH^- \rightarrow Mn(OH)_2$$

which rapidly becomes brown in the air, owing to the formation of manganous manganites, which are less soluble than $Mn(OH)_2$.

First a part of the manganous hydroxide is oxidized by the air to manganous acid:

$$2\,Mn(OH)_2 + O_2 \rightleftarrows 2\,H_2MnO_3$$

which, on coming in contact with the basic manganous hydroxide, immediately forms a salt with it — a manganite:

$$\mathbf{H_2MnO_3} + \mathbf{Mn(OH)_2} \rightleftarrows \mathbf{MnMnO_3} + 2\,H_2O$$

or possibly: $$2\,\mathbf{H_2MnO_3} + \mathbf{Mn(OH)_2} \rightleftarrows \mathbf{MnH_2(MnO_3)_2} + 2\,H_2O$$

This oxidation takes place in the air only gradually, but immediately in the presence of chlorine, bromine, hypochlorites, hydrogen peroxide, etc.:

$$\mathbf{Mn(OH)_2} + 2\,NaOH + Cl_2 \rightarrow 2\,NaCl + H_2O + \mathbf{H_2MnO_3}$$

$$\mathbf{Mn}(OH)_2 + H_2O_2 \rightarrow H_2O + \mathbf{H_2MnO_3}$$

Precipitated manganous acid dissolves in potassium acid oxalate solution forming a beautiful red solution of a complex mangano-oxalate ion.

The formation of manganites is of technical importance, as mentioned on page 220. The residue obtained in the preparation of chlorine from pyrolusite and hydrochloric acid consists chiefly of manganese chloride; by adding lime to it, manganous hydroxide is formed. This mixture of manganous hydroxide and lime is exposed to the action of the atmosphere, whereby manganous acid is formed, which unites with the calcium as the stronger base, forming calcium bimanganite, so that finally all the manganese is oxidized to manganous acid:

$$2\,\mathbf{Mn(OH)_2} + O_2 + Ca(OH)_2 \rightarrow 2\,H_2O + CaH_2(MnO_3)_2$$

On treating the residue, when in the right condition, with hydrochloric acid again, the same amount of chlorine is obtained as from the original pyrolusite:

$$2\,\mathbf{MnO_2} + 8\,HCl \rightarrow 4\,H_2O + 2\,MnCl_2 + 2\,Cl_2\uparrow$$

$$\mathbf{CaH_2(MnO_3)_2} + 10\,HCl \rightarrow 6\,H_2O + 2\,MnCl_2 + CaCl_2 + 2\,Cl_2\uparrow$$

It is necessary, however, to add a little more hydrochloric acid in the latter case, because a part of the acid is used up in setting the manganous acid free from the manganite.

2. **Ammonia** precipitates from neutral solutions free from ammonium salts (as with magnesium and ferrous salts) a part of the manganese as the white hydroxide:

$$MnCl_2 + 2\,NH_4OH \rightleftarrows \mathbf{Mn(OH)_2} + 2\,NH_4Cl$$

If sufficient ammonium chloride is present, ammonia causes no precipitation (cf. p. 271). The greater part of the manganese then remains in solution as manganous chloride, but a small amount exists as the hydroxide. On standing in the air, this dissolved $Mn(OH)_2$ is changed slowly into the more difficultly soluble manganous acid, H_2MnO_3, which is deposited in brown flocks. The condition of equilibrium in the solution is thereby disturbed, and in order to restore it more hydroxide is formed, and the reaction continues in this way until finally all the manganese may be precipitated. This fact must be considered in the separation of manganese from ferric iron, aluminum, etc. If a solution of ferric and manganous chlorides contains sufficient ammonium chloride, none of the manganese and all the iron will be precipitated on the addition of ammonia, but, if the solution stands in contact with the air, gradually the manganese will be precipitated. In effecting the separation, therefore, an excess of ammonium chloride should be present, the solution boiled to remove the air as much as possible from the solution, then a *slight* excess

of ammonia should be added and the solution filtered *immediately*. The separation even then is not quantitative, but is satisfactory for qualitative analysis.

Oxidizing agents in the presence of ammonia cause the precipitation of manganese as H_2MnO_3. Bromine is ordinarily used as the oxidizing agent, but a number of precautions are necessary to accomplish the complete precipitation of manganese by means of bromine and ammonia.

If a neutral solution of manganous salt is treated with bromine, the precipitation of manganese as H_2MnO_3 is always incomplete:

$$Mn^{++} + Br_2 + 3\,H_2O \rightleftarrows 4\,H^+ + 2\,Br^- + \mathbf{H_2MnO_3}$$

The precipitation of the manganese can be made complete, in accordance with the mass-action principle (p. 2), if the hydrogen ions formed in the reaction are neutralized; sodium bromide in neutral solution will not reduce H_2MnO_3, but hydrobromic acid will do so. The solution may be neutralized by caustic alkali, alkali carbonate, alkali acetate (cf. p. 49), or ammonia. A solution of manganous salt may contain a considerable excess of acetic acid and yet the manganese will be completely precipitated by bromine in the presence of sodium acetate.

Ammonia is not altogether satisfactory as a neutralizing agent in this case because it reacts with bromine as well as with hydrobromic acid. When bromine is added to ammonia solution, a vigorous reaction takes place and nitrogen is evolved:

$$8\,NH_3 + 3\,Br_2 \rightarrow 6\,NH_4Br + N_2\uparrow$$

When bromine is added to a solution of ammonium chloride a very slow oxidation results and nitrogen gas is evolved:

$$2\,NH_4^+ + 3\,Br_2 \rightleftarrows 8\,H^+ + 6\,Br^- + N_2\uparrow$$

If sodium acetate is added to this solution, the reaction is accelerated greatly as a result of diminishing the concentration of the hydrogen ions, and by heating the solution, which increases the speed of the reaction and causes the rapid expulsion of nitrogen gas, all the ammonium salt can be decomposed by means of a very slight excess of bromine.

The presence of ammonium salts prevents the precipitation of manganese by bromine and sodium acetate; when all the ammonium salt has been oxidized to nitrogen, the manganese can be precipitated as H_2MnO_3 provided the solution is not allowed to become acid.

The conditions are more favorable for the precipitation of manganese when the solution contains hydroxide ions, as in an ammoniacal solution. The addition of bromine to such a solution usually results in the immediate precipitation of some of the manganese but, as a result of the action of bromine on ammonia or ammonium salt, the solution usually becomes acid and the precipitation of the manganese is then incomplete. To precipitate all the manganese by means of ammonia and bromine, it is best to proceed as follows:

Dilute the solution to about 200 ml and neutralize, if necessary, with ammonia. Add a little bromine water and a slight excess of ammonia, and stir to promote the formation of a precipitate. Heat the solution, add a little more bromine water, and make slightly ammoniacal again. If the amount of the manganese precipitate is perceptibly increased by this last treatment with bromine and ammonia, repeat the operation. Filter off the precipitated H_2MnO_3, concentrate the solution somewhat by evaporation, and again treat with bromine water and ammonia. Sometimes H_2MnO_3 is precipitated on the sides of the vessel during evaporation. The

treatment with bromine and ammonia should be continued until a filtrate is obtained which will not give any more precipitate with these reagents.*

3. **Alkali Carbonates** precipitate white manganous carbonate,

$$Mn^{++} + CO_3^{--} \rightarrow \mathbf{MnCO_3}$$

which after long boiling is changed by the oxygen of the air into less soluble, hydrated manganese dioxide:

$$2\,\mathbf{MnCO_3} + 2\,H_2O + O_2 \rightarrow 2\,CO_2\uparrow + \mathbf{2\,H_2MnO_3}$$

4. **Alkali Hypobromite and Copper Salt.** The hyprobromite anion in alkaline solutions causes the precipitation of black manganese dioxide. If, however, a little Cu^{++} is present the oxidation goes farther and instead of a dark brown precipitate a violet permanganate solution is obtained:

$$2\,Mn^{++} + 5\,BrO^- + 6\,OH^- \rightarrow 2\,MnO_4^- + 5\,Br^- + 3\,H_2O$$

Probably a little $Cu(OH)_2$ is precipitated first by the OH^- ions and at the surface of the precipitate there is a catalyzed decomposition of the OBr^- anion into Br^- and atomic oxygen which accomplishes the oxidation of the Mn^{++} to MnO_4^-. Cobalt and nickel have a similar but not so strong catalytic effect. The presence of chromium interferes with this test since yellow CrO_4^{--} ions are formed which make it difficult to see the purple MnO_4^-. The test is not as sensitive as the persulfate or bismuthate tests which are made in acid solutions.

Procedure.— Place 2 ml of 1 per cent copper sulfate solution in a small test tube, add 1 drop of the solution to be tested and 8–10 ml of 0.1 *N* NaBrO solution. After gently boiling, the liquid above the precipitate will show the permanganate color if 2.5 γ of manganese is present. Another way of carrying out the test is the following: Place 10 ml of the acid solution to be tested in a small test tube; add 1 drop of saturated copper sulfate solution and about 0.5 g of a mixture of 0.2 g $KBrO_3$ and 0.3 g KBr. The test will be obtained if 3 γ of manganese is present in the 10 ml of solution.

5. **Ammoniacal Silver Nitrate** reacts with Mn^{++} to give a precipitate of MnO_2 and finely divided Ag:

$$Mn^{++} + 2\,[Ag(NH_3)_2]^+ + 4\,OH^- \rightarrow \mathbf{MnO_2} + 2\,\mathbf{Ag} + 4\,NH_3 + 2\,H_2O$$

Place a drop of the solution upon filter paper; add a drop of saturated silver nitrate solution which has been treated with concentrated ammonia solution until the precipitate of silver hydroxide has dissolved and then with the same quantity of ammonia in addition. A blackening will be observed, especially on heating, if 0.7 γ of manganese is present.

6. **Ammonium Carbonate** precipitates the white carbonate even in the presence of ammonium salts (difference from magnesium).

7. **Ammonium Persulfate** added to a hot solution of Mn^{++} in dilute sulfuric or nitric acid causes gradual precipitation of hydrated MnO_2.

* The above explanation is given at length because of its importance in quantitative analysis. The facts upon which the explanation is based have been carefully verified by quantitative experiments performed by S. G. Simpson at the Massachusetts Institute of Technology.

If, however, the solution contains some Ag^+ as catalyst, the oxidation goes farther and MnO_4^- is formed:

$$2\,Mn^{++} + 5\,S_2O_8^{--} + 8\,H_2O \rightarrow 16\,H^+ + 10\,SO_4^{--} + 2\,MnO_4^-$$

This reaction is quantitative for small amounts of manganese and in the absence of anything that will react with the permanganic acid.*

To carry out the test on a small scale, take 1 drop of solution to be tested in a tiny porcelain crucible, add 1 drop of concentrated H_2SO_4, a drop of $AgNO_3$ solution, and a little solid $(NH_4)_2S_2O_8$. Heat gently and a violet coloration will appear if 0.1 γ of manganese is present (Feigl).

8. **Ammonium Sulfide** precipitates from manganese solutions flesh-colored, hydrated manganese sulfide:

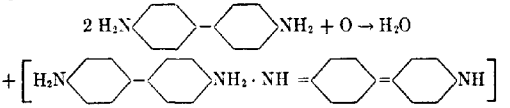
$$Mn^{++} + S^{--} \rightarrow \mathbf{MnS}$$

On boiling with a large excess of ammonium sulfide it is changed into less hydrated *green* manganese sulfide of the formula $3\,MnS \cdot H_2O$.

The solubility product of MnS is relatively large (cf. p. 23), and to precipitate all the manganese as sulfide an excess of S^{--} ions is necessary. The precipitate dissolves readily in dilute acid as a result of the removal of the S^{--} ions to form non-ionized hydrogen sulfide (cf. p. 51).

9. **Barium Carbonate** produces a precipitate only in hot solutions.

10. **Benzidine**, $C_{12}H_8(NH_2)_2$, gives a blue oxidation product in alkaline solution when manganese is present:



The manganous cations react with OH^- to form $Mn(OH)_2$, which is oxidized rapidly by dissolved oxygen gas forming MnO_2 which oxidizes the benzidine. The test can be obtained with 0.15 γ of manganese.

11. **Lead Peroxide** and **Concentrated Nitric Acid.** (Volhard's reaction). — If a solution containing only traces of manganese is boiled with lead peroxide and concentrated nitric acid, then diluted with water and the residue allowed to settle, the supernatant liquid acquires a distinct violet-red color, owing to the formation of permanganic acid:

$$2\,Mn^{++} + 5\,PbO_2 + 4\,H^+ \rightarrow 5\,Pb^{++} + 2\,H_2O + 2\,MnO_4^-$$

This extremely delicate reaction does not take place in the presence of much hydrochloric acid or chlorides, because the permanganic acid is thereby destroyed:

$$2\,HMnO_4 + 14\,HCl \rightarrow 8\,H_2O + 2\,MnCl_2 + 5\,Cl_2\uparrow$$

* Cf. M. Marshall, *Z. anal. Chem.*, **43**, 418, 655 (1904).

12. **Periodate and Arnold's Base.** Arnold's base, tetramethyldiaminodiphenyl methane, $(H_3C)_2N-C_6H_4-CH_2-C_6H_4-N(CH_3)_2$, is prepared by the action of formaldehyde (formalin) on a solution of dimethyl aniline in methyl alcohol and concentrated hydrochloric acid. As reagent, a 1 per cent solution of the *tetra* base in chloroform is used.

Place a drop of the solution to be tested on a spot plate and add in succession 1 drop of a saturated solution of KIO_4, 1 drop of 2 *N* acetic acid and 2 drops of the chloroform solution of the base. If manganese is present, the chloroform is colored an intense blue owing to the formation of an oxidation product of the base. Chromium must be absent as it will be oxidized to chromate which gives the same test. The test is exceedingly delicate and will take place with only 0.001 γ of manganese.

13. **Oxidizing Agents** added to a saturated solution of manganous chloride in concentrated hydrochloric acid give, on heating, a deep brown or black coloration due to the formation of manganese tetrachloride. The reaction is given by a nitrate, chlorate, hypochlorite, or chromate, and by lead peroxide. It fails with perchlorate, bromate, bromine, sodium peroxide, persulfate, nitrite, and red lead.*

14. **Potassium Bromate** added to a cold sulfuric acid solution of a manganous salt gives the violet color of permanganate. The chlorate and iodate do not give the reaction.

15. **Potassium Chlorate.** — By boiling a solution of manganous salt in concentrated nitric acid with an excess of potassium chlorate, all the manganese is precipitated as MnO_2:

$$Mn(NO_3)_2 + 2\,KClO_3 \rightarrow \mathbf{MnO_2} + 2\,KNO_3 + 2\,ClO_2\uparrow$$

16. **Potassium Cyanide.** — On adding potassium cyanide to a solution of a manganous salt, a brown precipitate appears which dissolves in an excess of potassium cyanide, forming a brown solution. On standing, or by heating the solution, a voluminous green precipitate of $K[Mn(CN)_3]$ is formed which is soluble in strong potassium cyanide solution:

$$Mn^{++} + 2\,CN^- \rightleftarrows \mathbf{Mn(CN)_2},\ \mathbf{Mn(CN)_2} + KCN \rightleftarrows \mathbf{K[Mn(CN)_3]}$$
$$\mathbf{K[Mn(CN)_3]} + 3\,CN^- \rightleftarrows K^+ + [Mn(CN)_6]^{---}$$

To keep the managanese in solution in the form of $Mn(CN)_6^{---}$ ions, it is necessary to use an excess of potassium cyanide. If the concentration of the cyanide is diminished by dilution, some green $K[Mn(CN)_3]$ is formed, and if the dilute cyanide solution is boiled, a precipitate of $Mn(OH)_2$ results:

$$[Mn(CN)_6]^{---} + 2\,H_2O \rightleftarrows 2\,HCN + 4\,CN^- + \mathbf{Mn(OH)_2}$$

The stability of these complex cyanides, therefore, is much less than that of the corresponding nickel compounds (p. 236). This permits an interesting method of separating nickel from manganese.

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* De Koninck, *Z. anal. Chem.*, **43**, 418.

Nickel sulfide is much less soluble than manganous sulfide (cf. p. 23) so that it is possible to precipitate nickel as sulfide in the presence of acetic acid and sodium acetate; under these conditions no manganese sulfide is formed. If, on the other hand, ammonium sulfide is added to a hot, dilute solution containing the complex cyanides of nickel and manganese, the nickel will remain in solution and the precipitation of the manganese as sulfide will be complete:

$$[Mn(CN)_6]^{--} + S^{--} \rightleftarrows 6\,CN^- + \mathbf{MnS}$$

In the presence of a large excess of potassium cyanide, however, the $[Mn(CN)_6]^{--}$ anion is so stable that none of the manganese is precipitated in the cold by ammonium sulfide.

17. **Potassium Ferricyanide** forms brown manganous ferricyanide, $Mn_3[Fe(CN)_6]_2$, slightly soluble in cold hydrochloric acid and insoluble in ammonia.

18. **Potassium Ferrocyanide** precipitates white manganous ferrocyanide, $Mn_2[Fe(CN)_6]$, which is difficultly soluble in hydrochloric acid. The precipitate can be obtained also in a solution which has been treated with tartaric acid and ammonia.

19. **Potassium Periodate** gives a deep red precipitate, or a red color with dilute solutions; manganous periodate is probably formed. Hydrochloric acid dissolves the precipitate with evolution of chlorine; caustic soda, and even ammonia, changes it into black manganous acid, H_2MnO_3. The reaction is delicate and is aided by heating.

20. **Sodium Bismuthate** added to a cold solution of a manganous salt in dilute nitric acid (about density 1.13) causes the formation of permanganic acid. The reagent, which corresponds approximately to the formula $NaBiO_3$, is prepared by fusing bismuth oxide with sodium peroxide; it is insoluble in water, and the excess of reagent may be filtered off through asbestos after applying the test. The reaction may be expressed by the equation:

$$2\,Mn^{++} + 5\,\mathbf{NaBiO_3} + 16\,H^+ \rightarrow 5\,Na^+ + 5\,Bi^{+++} + 7\,H_2O + 2\,HMnO_4$$

The test is extremely delicate when nothing is present that will react with the permanganate formed. An insoluble carbonaceous residue, such as remains after the solution of cast iron in acid, must be filtered off before adding the reagent. If the solution is heated, the permanganic acid breaks down and hydrated manganese dioxide is precipitated.

Bismuth dioxide, BiO_2, may he used instead of sodium bismuthate.

21. **Sodium Phosphate** precipitates white, tertiary manganous phosphate,

$$4\,HPO_4^{--} + 3\,Mn^{++} \rightarrow 2\,H_2PO_4^- + \mathbf{Mn_3(PO_4)_2}$$

soluble in mineral acids and in acetic acid:

$$\mathbf{Mn_3(PO_4)_2} + 2\,H^+ \rightleftarrows 3\,Mn^{++} + 2\,HPO_4^{--}$$

If the boiling solution of this precipitate in acid is neutralized with ammonia, manganous ammonium phosphate will be precipitated, as

with magnesium (see p. 273):

$$HPO_4^{--} + NH_4OH \rightleftarrows NH_4^+ + PO_4^{---} + H_2O$$
$$Mn^{++} + NH_4^+ + PO_4^{---} + 7\,H_2O \rightarrow \mathbf{MnNH_4PO_4 \cdot 7\,H_2O}$$

The crystalline precipitate is flesh colored and is practically insoluble in water.

Reactions in the Dry Way

The borax and salt of phosphorus beads are amethyst red after heating in the oxidizing flame with small amounts of manganese, almost brown with larger amounts, and can then be mistaken for the nickel bead. Heated in the reducing flame, the manganese bead becomes colorless, while the nickel bead appears gray.

On fusing any manganous compound with caustic alkali or alkali carbonate (on platinum foil) in the air, or, better still, in the presence of an oxidizing agent (such as potassium nitrate, potassium chlorate, etc.), a green melt is obtained, owing to the formation of the alkali salt of manganic acid, as is shown by the following equations:

$$MnO + Na_2CO_3 + O_2 \rightarrow CO_2\uparrow + Na_2MnO_4$$
$$2\,MnO_2 + 2\,Na_2CO_3 + O_2 \rightarrow 2\,CO_2\uparrow + 2\,Na_2MnO_4$$
$$2\,Mn_2O_3 + 4\,Na_2CO_3 + 3\,O_2 \rightarrow 4\,CO_2\uparrow + 4\,Na_2MnO_4$$
$$2\,Mn_3O_4 + 6\,Na_2CO_3 + 5\,O_2 \rightarrow 6\,CO_2\uparrow + 6\,Na_2MnO_4$$
$$MnSO_4 + 2\,Na_2CO_3 + O_2 \rightarrow 2\,CO_2\uparrow + Na_2SO_4 + Na_2MnO_4$$

The oxygen comes either from the air or from the nitrate or chlorate:

$$2\,KNO_3 \rightarrow 2\,KNO_2 + O_2\uparrow, \quad 2\,KClO_3 \rightarrow 2\,KCl + 3\,O_2\uparrow$$

This reaction is exceedingly delicate; a fraction of a milligram of any manganese compound can be recognized by the formation of this green color.

By ignition in the air the oxides of manganese are changed to Mn_3O_4:

$$6\,MnO + O_2 \rightarrow 2\,Mn_3O_4, \quad 3\,MnO_2 \rightarrow Mn_3O_4 + O_2\uparrow,$$
$$6\,Mn_2O_3 \rightarrow 4\,Mn_3O_4 + O_2\uparrow$$

B. Manganates and Permanganates

Free manganic acid has never been isolated. If we attempt to form it from the green melt of the alkali manganate by the addition of acid, permanganic acid and hydrated manganese dioxide will be obtained; a part of the unstable manganic acid oxidizes another part of the same to permanganic acid, while the oxidizing part is itself reduced to hydrated manganese dioxide:

$$3\,H_2MnO_4 \rightarrow 2\,HMnO_4 + H_2MnO_3 + H_2O$$

This transformation takes place so readily that the green solution of the manganate is changed to a reddish violet solution of a permanganate by simply standing in the air, with the help of the carbonic acid which the air always contains:

$$3\ K_2MnO_4 + 2\ CO_2 + H_2O \rightarrow 2\ K_2CO_3 + H_2MnO_3 + 2\ KMnO_4$$

The reaction takes place much more rapidly, however, if a few drops of a strong acid are added.

The oxidation of one molecule at the expense of another of the same kind is of quite common occurrence in chemistry. It always involves a loss in the *available* or *free energy* which the molecules originally possessed. The total energy possessed by any molecule can be considered to consist partly of free energy and partly of unavailable energy. *A reaction that takes place spontaneously is always characterized* by the fact that the free energy of the system is less afterward than it was before the reaction took place. The condition with the smallest free energy is the most stable condition.

It might be inferred that the most stable conditions are those having the smallest quantities of energy, but a little consideration shows that in promoting chemical reactions it is not so much the total energy as it is the available energy which comes into consideration. Thus, a vast amount of energy is stored up in the heat of the ocean, but it is not available energy, because it is in surroundings at the same temperature. The air under ordinary atmospheric pressure could perform a great deal of work if it were brought in contact with a space in which a much lower gas pressure prevailed, but otherwise the vast amount of energy is not available.

In the changes that take place with any given element it is not necessarily true that an increase in the total energy will always involve an increase in the free energy associated with the element. The fact that the solution of a manganate, in which the valence of the manganese is six, decomposes readily indicates merely that the free energy in the system composed of quadrivalent and heptavalent manganese is less than the free energy involved in the system containing all the manganese in the hexavalent condition. Frequently the conditions are just the reverse, and the most stable condition is one of intermediate valence. Thus permanganate and manganous salt react to form quadrivalent manganese. A few reactions similar to the decomposition of H_2MnO_4 will be given.

Hypochlorites are changed, by warming the aqueous solution, into chlorate and chloride; one atom of chlorine is oxidized from the valence of one to the valence of five at the expense of two atoms of chlorine, which are reduced from a positive valence of one to a negative valence of one:

$$3\ ClO^- \rightarrow ClO_3^- + 2\ Cl^-$$

Ignition of a chlorate causes the formation of a perchlorate, a chloride, and free oxygen. Here one atom of chlorine is increased two in valence, one atom of chlorine loses six charges, and the remaining four charges cause the oxidation of two atoms of negatively charged oxygen:

$$2\ NaClO_3 \rightarrow NaClO_4 + NaCl + O_2\uparrow$$

Nitrous acid is changed in aqueous solution into nitric acid and nitric oxide, one atom of nitrogen gaining two charges and two similar atoms losing one charge:

$$2\ H^+ + 3\ NO_2^- \rightarrow NO_3^- + 2\ NO\uparrow + H_2O$$

Hypophosphorous acid and also phosphorous acid can be changed into phosphoric acid and phosphine:

$$2\ H_3PO_2 \rightarrow H_3PO_4 + PH_3\uparrow \qquad 4\ H_3PO_3 \rightarrow 3\ H_3PO_4 + PH_3\uparrow$$

Alkali thiosulfates and alkali sulfites are changed by ignition into sulfate and sulfide:

$$4\ Na_2S_2O_3 \rightarrow 3\ Na_2SO_4 + Na_2S_5, \quad 4\ Na_2SO_3 \rightarrow 3\ Na_2SO_4 + Na_2S$$

Permanganic Acid, $HMnO_4$, although much more stable than manganic acid, is known only in aqueous solution; but the anhydride Mn_2O_7 has been isolated. On cautiously adding concentrated sulfuric acid to the cooled solution of a permanganate, oily drops of reddish brown Mn_2O_7 separate out, which, however, on being warmed (the heat of reaction is sufficient), explode with scintillation:

$$2\ Mn_2O_7 + 4\ H_2SO_4 \rightarrow 4\ MnSO_4 + 4\ H_2O + 5\ O_2\uparrow$$

All the salts of permanganic acid (the permanganates) are soluble in water, with a reddish violet color, and are very energetic oxidizing agents. In acid solution the heptavalent manganese in permanganate is usually reduced to bivalent manganous salt, but in alkaline, or nearly neutral, solutions quadrivalent manganese as the dioxide is the usual product.

By heating solid potassium permanganate to 240° C, potassium manganate and MnO_2 are formed, also with evolution of oxygen:

$$2\ KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2\uparrow$$

Oxidation in Acid Solution. — Typical oxidation equations with permanganate have already been explained on page 34. A few of these reactions will be repeated here, but it will not be necessary to enter into further details concerning the method of balancing the equations. To avoid exact repetition, the equations will be given with the entire molecules written instead of merely the ions involved:

$$2\ KMnO_4 + 3\ H_2SO_4 + 10\ HCl \rightarrow K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ Cl_2\uparrow$$

$$2\ KMnO_4 + 3\ H_2SO_4 + 10\ HI \rightarrow K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ I_2$$

$$2\ KMnO_4 + 3\ H_2SO_4 + 5\ H_2S \rightarrow K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ S$$

$$8\ KMnO_4 + 12\ H_2SO_4 + 5\ PH_3 \rightarrow 4\ K_2SO_4 + 8\ MnSO_4 + 12\ H_2O + 5\ H_3PO_4$$

$$2\ KMnO_4 + 6\ SO_2 + 2\ H_2O \rightarrow 2\ KHSO_4 + 2\ MnSO_4 + H_2S_2O_6$$

In this last equation the proportion of sulfate and of dithionic acid, $H_2S_2O_6$, will vary with the temperature and concentration of the solution:

$$2\ KMnO_4 + 5\ H_2C_2O_4 + 3\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + 10\ CO_2\uparrow$$

$$2\ KMnO_4 + 5\ H_2O_2 + 4\ H_2SO_4 \rightarrow 2\ KHSO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ O_2\uparrow$$

$$2\ KMnO_4 + 5\ K_2C_2O_6 + 14\ H_2SO_4 \rightarrow$$

$$12\ KHSO_4 + 2\ MnSO_4 + 8\ H_2O + 10\ CO_2\uparrow + 5\ O_2\uparrow$$

Persulfuric acid, which is analogous to percarbonic acid, does not reduce a solution of a permanganate. An interesting reaction is that

which takes place in nearly neutral solution between permanganate and manganous ions. The principal product is MnO_2, which will carry down some of the bivalent manganese as manganous manganite unless an excess of some other ion is present which forms an insoluble manganite, *e.g.*, zinc or calcium ions:

$$2\,KMnO_4 + 3\,MnSO_4 + 2\,H_2O \rightarrow 2\,KHSO_4 + 5\,\mathbf{MnO_2} + H_2SO_4$$

Oxidation in Alkaline Solution. — Many *organic* substances are oxidized by permanganates in alkaline solution with precipitation of manganese dioxide. Thus formic acid is oxidized to carbonic acid, ethyl alcohol to aldehyde and acetic acid, and cellulose (paper) chiefly to oxalic acid, so that a solution of a permanganate cannot be filtered through paper. By boiling a concentrated solution of potassium permanganate with concentrated potassium hydroxide, potassium manganate is formed with evolution of oxygen, and the color of the solution becomes green:

$$4\,KMnO_4 + 4\,KOH \rightarrow 4\,K_2MnO_4 + 2\,H_2O + O_2\uparrow$$

NICKEL, Ni. At. Wt. 58.69, At. No. 28.

Density 8.9. M. P. 1452°. B. P. 2900°

Occurrence. — In the native state nickel occurs only in meteorites. It is most frequently found in combination with sulfur, arsenic, and antimony in regular and hexagonal crystallizing minerals, of which the following are the most important: *Isometric System*: Chloanthite, $NiAs_2$; gersdorffite, NiAsS; ullmannite, NiSbS. *Hexagonal System*: Niccolite, Ni_2As_2; breithauptite, Ni_2Sb_2; millerite, Ni_2S_2.

Nickel also occurs as regular crystals of bunsenite, NiO, isomorphous with periclasite, MgO, and manganosite, MnO; as garnierite or noumeite, $H_2(NiMg)SiO_4$ + aq, a mineral occurring in New Caledonia, from which pure nickel can be prepared; and finally as annabergite, $Ni_3(AsO_4)_2 \cdot 8\,H_2O$, isomorphous with erythrite.

Properties. — Nickel is a hard, silvery white metal which takes a high polish. Its name probably is derived from the German word *Nikker* = devil, which corresponds to our "Old Nick" and can be traced to superstition among miners. It was discovered by Cronstedt in 1751. The metal is malleable, ductile, and very tenacious. It is harder than pure iron and does not oxidize in dry or moist air at ordinary temperatures so that nickel plating of metals is a common practice. Nickel is magnetic but loses its magnetism above 345°. Important alloys of nickel are: nickel steel, containing up to 5 per cent nickel or more; chrome nickel steel, containing 1 per cent chromium and 3 per cent nickel; "invar," an alloy with 36 per cent nickel which has a very low coefficient of expansion; "permalloy," with 80 per cent nickel, which is used as sheathing for electric cables and has a magnetic permeability 200 times as great as pure iron; monel metal, with 2 parts nickel to 1 part copper with a little iron and manganese; nichrome, which has 11–25 per cent chromium, up to 25 per cent iron, and the rest nickel; and German silver, 50–65 per cent copper, 10–30 per cent nickel, and the balance zinc. Finely divided nickel will absorb 17 times its own volume of hydrogen gas and, for this reason, is used in numerous hydrogenation

processes. Nickel dissolves with difficulty in hydrochloric and sulfuric acids but dissolves readily in dilute nitric acid. It becomes passive with concentrated nitric acid.

Oxides and Hydroxides. — Green or grayish green nickel oxide, NiO, is obtained when the carbonate, nitrate, or hydroxide of nickel is heated. The light green hydroxide, $Ni(OH)_2$, is formed by adding alkali hydroxide to a nickel solution. Iron, cobalt, and nickel are closely related elements and occur in the eighth group of the periodic table as elements 26, 27, and 28. One would expect that nickel, like iron, would form the oxides Ni_2O_3 and Ni_3O_4. The existence of these oxides has, however, been doubted by some, and it is claimed that $NiO_2 \cdot H_2O$, instead of $Ni(OH)_3$, is formed when a nickelous solution is treated with caustic alkali and halogen. We shall assume here that brownish black nickelic oxide, Ni_2O_3, exists.

By dissolving either oxide of nickel in acid, salts of bivalent nickel are always obtained:

$$NiO + 2\,HCl \rightarrow H_2O + NiCl_2$$

$$Ni_2O_3 + 6\,HCl \rightarrow 3\,H_2O + 2\,NiCl_2 + Cl_2\uparrow$$

$$2\,Ni_2O_3 + 4\,H_2SO_4 \rightarrow 4\,H_2O + 4\,NiSO_4 + O_2\uparrow$$

Nickelous oxide behaves as a basic anhydride, but nickelic oxide acts as a peroxide and forms no salts.

The crystallized salts of nickel and their aqueous solutions are green, but in the anhydrous condition they are usually yellow. Most of the salts are soluble in water; the sulfide, carbonate, and phosphate are insoluble.

Reactions in the Wet Way

1. **Alkali Hydroxide** precipitates apple-green nickelous hydroxide,

$$Ni^{++} + 2\,OH^- \rightarrow \mathbf{Ni(OH)_2}$$

insoluble in excess of the precipitant, readily soluble in acids.

Boiling the solution and adding hydrogen peroxide or iodine does not serve to oxidize the nickelous hydroxide, but bromine water, sodium hypochlorite, potassium ferricyanide, or a persulfate changes it to black nickelic hydroxide.

The presence of non-volatile organic acids and sugar prevents the precipitation of the bivalent and trivalent nickel hydroxides.

Nickelous hydroxide dissolves in ammonium carbonate solution giving a greenish blue liquid and in potassium cyanide to form potassium nickelocyanide. It also dissolves slowly in a mixture of ammonia and ammonium chloride forming nickelous-ammonia complex ions (ammines).

2. **Ammonia** precipitates (in neutral solutions free from ammonium salts) a green basic salt,

$$2\,NiSO_4 + 2\,NH_4OH \rightarrow (NH_4)_2SO_4 + \mathbf{Ni_2SO_4(OH)_2}$$

soluble (with a blue color) in excess of ammonia, forming complex nickel ammonia ions (cf. p. 28).

$$\mathbf{Ni_2SO_4(OH)_2} + 12\,NH_3 \rightarrow 2\,[Ni(NH_3)_6]^{++} + 2\,OH^- + SO_4^{--}$$

In the presence of sufficient ammonium salt, ammonia produces no precipitate, as with magnesium, ferrous and manganous salts; potassium and sodium hydroxides, however, precipitate the green hydroxide (difference from cobalt, see p. 239).

The anhydrous chloride and sulfate readily absorb ammonia, forming anhydrous nickelous ammines:

$$NiCl_2 + 6\ NH_3 \rightarrow [Ni(NH_3)_6]Cl_2;\ NiSO_4 + 6\ NH_3 \rightarrow [Ni(NH_3)_6]SO_4$$

The nickel ammonia cations are very stable in the presence of an excess of ammonia. In pure water they are in equilibrium with a small quantity of nickel ions, dissolved ammonia, and ammonium hydroxide:

$$[Ni(NH_3)_6]^{++} \rightarrow Ni^{++} + 6\ NH_3;\ NH_3 + H_2O \rightarrow NH_4OH$$

3. **Ammonium Carbonate** behaves similarly, but the precipitate is soluble in an excess of the precipitant, forming hexamminenickelous carbonate.

4. **Ammonium Molybdate** in neutral or slightly acid solutions of nickel salts causes a greenish white precipitation on heating to 70°.

5. **Ammonium Sulfide** precipitates from neutral solutions the nickel as sulfide:

$$NiCl_2 + (NH_4)_2S \rightarrow 2\ NH_4Cl + NiS$$

Nickel sulfide has a marked tendency to form colloidal solutions of a dark brown color, especially in the presence of ammonia or a considerable excess of ammonium sulfide. By making the brown solution slightly acid with acetic acid and boiling, the hydrosol is coagulated and can be removed by filtration. The presence of ammonium salts also favors the coagulation of the hydrosol.

If it is desired to precipitate the nickel as sulfide from an ammoniacal solution, it is best to make the solution very slightly acid, add a little ammonium chloride unless considerable is already present, heat to boiling, add colorless ammonium sulfide drop by drop until no further precipitation takes place, and then add 0.5 to 1 ml of the reagent in excess. The nickel sulfide thus obtained can be filtered without difficulty, and the filtrate is free from nickel. During the filtration care should be taken to keep the filter well filled with liquid to prevent the oxidation of the precipitate, which takes place readily on exposure to the air. To wash the precipitate it is well to use a hot 5 to 10 per cent ammonium chloride solution to which a little colorless ammonium sulfide has been added. The washing can also be effected with hydrogen sulfide water without there being any danger of hydrosol formation.

Nickel sulfide is difficultly soluble in dilute mineral acids, readily soluble, however, in strong nitric acid or in aqua regia, with separation of sulfur:

$$3\ NiS + 6\ HCl + 2\ HNO_3 \rightarrow 3\ NiCl_2 + 2\ NO\uparrow + 4\ H_2O + 3\ S$$

The sulfur usually separates out as a black film. This is caused by the sulfur first melting, owing to the heat of reaction, enclosing small particles of the black

sulfide and protecting them from the action of the acid. By continued action of the acid all the sulfide is dissolved, and the sulfur remains as yellow drops, which are oxidized little by little to sulfuric acid:

$$S + 2\,HNO_3 \rightarrow H_2SO_4 + 2\,NO\uparrow$$

Nickel and cobalt sulfides, though not precipitated by hydrogen sulfide from a dilute hydrochloric acid solution, dissolve with difficulty in a much stronger acid. This is perhaps due to the fact that these sulfides exist in two allotropic forms of different solubilities. The sulfide first precipitated is readily soluble in acid, but on standing it becomes changed into a much more insoluble condition. Most schemes of qualitative analysis are based upon this behavior; the nickel and cobalt are separated from zinc and manganese by treating the ammonium sulfide precipitate with cold, dilute hydrochloric acid. In such cases some nickel and cobalt always pass into solution and the quantity dissolved may be much larger than is ordinarily assumed. If the surface exposed to the action of the acid is large, or if left in a finely divided state by the dissolving out of other sulfide, a considerable quantity of nickel dissolves in a comparatively short time. The reverse reaction, the precipitation of nickel sulfide by hydrogen sulfide in very dilute acid solution, also takes place very slowly but continuously.*

6. Villiers has developed a very sensitive test which depends upon the formation of a brown colloidal solution of nickel sulfide. The nickel salt solution is treated with tartaric acid and a slight excess of sodium hydroxide and is then saturated with hydrogen sulfide: a part of the nickel always remains in solution and colors it dark brown. Cobalt ions are precipitated as cobalt sulfide by this treatment except when only a trace of cobalt is present, when it is likely to give a brown color; caustic soda, however, causes the cobalt sulfide to precipitate.

7. **Ammonium Thioacetate** precipitates nickel sulfide from ammoniacal solution. In an acid solution, sodium thiosulfate has no effect, but in neutral or alkaline solutions, nickel sulfide is slowly precipitated.

8. **Barium Carbonate** in the cold produces no precipitation; but by continued boiling, all the nickel is thrown down as basic carbonate.

9. **Dicyandiamidine Sulfate,** in 10 per cent aqueous solution, gives a yellow, crystalline precipitate of nickel dicyandiamidine, $(C_2H_5N_4O)_2Ni \cdot 2\,H_2O$. The reaction is a little slow in starting but the test is sensitive and characteristic. If the nickel solution is ammoniacal at the start, and contains ammonium chloride, then, after adding the reagent, the blue color is at once changed to yellow upon the addition of caustic soda and the precipitate forms gradually.

10. **Dimethylglyoxime,** $C_4H_8N_2O_2$ or $CH_3 \cdot C(NOH) \cdot C(NOH) \cdot CH_3$. —The reagent is prepared by dissolving 1 g of the solid in 100 ml of 98 per cent alcohol. If a little of the reagent is added to a solution of a nickel salt, then ammonia to give a slightly alkaline reaction, and the

* Cf. Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, **1908.**

solution is boiled, a red crystalline precipitate of the nickel salt of dimethylglyoxime is formed:

$$2\ \begin{matrix} CH_3 - C = NOH \\ | \\ CH_3 - C = NOH \end{matrix} + Ni^{++} + 2\ NH_3 \rightarrow 2\ NH_4^+ + (C_4H_7N_2O_2)_2Ni$$

If the quantity of nickel present is very small, at first a yellowish solution is obtained from which, on cooling, red needles are deposited. As little as 0.16 γ of nickel can be detected in 300,000 parts of water. The reaction is not influenced by the presence of ten times as much cobalt; when a larger proportion of cobalt is present, the following procedure is recommended:

DETECTION OF TRACES OF NICKEL IN COBALT SALTS

Add strong ammonia to the solution of the cobalt salt until a clear solution is obtained, then add a few milliliters of hydrogen peroxide and boil the solution a few minutes to decompose the excess of this reagent. Then add the dimethylglyoxime and again bring the solution to a boil. A very small quantity of nickel causes a red scum to form, and the glass sides of the beaker become coated with a film of red crystals. With smaller amounts of nickel the color is best observed upon the filter through which the solution is poured and the residue washed with hot water.

The above reaction is the most sensitive test known for detecting nickel in the presence of cobalt.

V. Fortini* recommends the following method for detecting nickel in alloys:

Heat the metal, from which all greasy or oily matter has been removed, at one spot with the oxidizing flame of the blowpipe. Cool and moisten with 1 drop of a solution of 0.5 g dimethylglyoxime in 5 ml alcohol and 5 ml concentrated ammonium hydroxide. A red spot at once appears if nickel is present. When copper is present, the nickel test is obtained before the copper ammonia color is visible.

The nickel test can be made in the presence of ferric iron if sufficient tartaric acid is added to prevent the precipitation of ferric hydroxide by ammonium hydroxide. The presence of ferrous iron interferes; it uses up the reagent and gives a very dark-colored solution.

11. **Hydrogen Sulfide** precipitates no nickel from solutions which contain mineral acid or much acetic acid; but from solutions slightly acid with acetic acid and containing an alkali acetate, all the nickel is precipitated as the black sulfide:

$$Ni^{++} + 2\ C_2H_3O_2^- + H_2S \rightarrow 2\ HC_2H_3O_2 + NiS$$

12. **Hydrorubianic Acid** forms in ammoniacal solutions a bluish violet complex salt with nickel.

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* *Chem. Ztg.*, **36**, 1461 (1912).

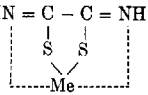
Hydrorubianic acid, $\begin{matrix} SC-NH_2 \\ | \\ SC-NH_2 \end{matrix}$, is the diamide of dithio-oxalic acid. When placed in solution it undergoes to some extent a rearrangement of the atoms in the molecule, and a tautomeric form (di-imido form) is in equilibrium with the original diamide,

$$\begin{matrix} SC-NH_2 \\ | \\ SC-NH_2 \end{matrix} \rightarrow \begin{matrix} HSC=NH \\ | \\ HSC=NH \end{matrix}$$

The new form is a di-imide and ionizes as a weak acid

$$\begin{matrix} HSC=NH \\ | \\ HSC=NH \end{matrix} \rightarrow 2\,H^+ + \left[\begin{matrix} SC=NH \\ | \\ SC=NH \end{matrix}\right]^{--}$$

In alkaline solutions, the H^+ is neutralized by OH^- and the above transformations take place more completely in the direction left to right. The anion of the acid forms characteristic compounds with copper, cobalt, and nickel. The precipitates correspond to the general formula:



in which Me is either copper, cobalt, or nickel. The precipitates formed in strongly ammoniacal solutions are insoluble in dilute mineral acids. The following test will detect 0.012 γ of nickel in 0.015 ml of solution.

Place 1 drop of the solution to be tested upon filter paper, hold the paper over the fumes of a bottle containing concentrated ammonia water, and then add 1 drop of a 1 per cent solution of hydrorubianic acid in alcohol. If nickel is present a blue-violet spot or a violet ring is obtained.

13. **α-Nitroso-β-naphthol,** dissolved in 50 per cent acetic acid, gives a brown precipitate of the following composition: $[C_{10}H_6O(NO)]_2Ni$. The precipitate dissolves in hydrochloric acid.

14. **Potassium Chromate** reacts only slowly with a cold, neutral solution of a nickel salt. At the boiling temperature a chocolate-brown basic chromate, $NiCrO_4 \cdot NiO$, is formed which dissolves easily in acid or in ammonia water.

15. **Potassium Cyanide** produces a light green precipitate of nickelous cyanide readily soluble in an excess of the precipitant, forming potassium nickelocyanide:

$$Ni^{++} + 2\,CN^- \rightarrow Ni(CN)_2$$
$$Ni(CN)_2 + 2\,CN^- \rightarrow [Ni(CN)_4]^{--}$$

The $[Ni(CN)_4]^{--}$ anion is a stable complex, but it is decomposed by the addition of acid, because $H_2[Ni(CN)_4]$ is a very weak acid and, like carbonic acid, is unstable:

$$[Ni(CN)_4]^{--} + 2\,H^+ \rightleftarrows H_2[Ni(CN)_4]$$
$$H_2[Ni(CN)_4] \rightleftarrows 2\,HCN + Ni(CN)_2$$

In alkaline solutions, containing an excess of cyanide, the $[Ni(CN)_4]^{--}$ anion is not dissociated to a sufficient extent into simple Ni^{++} cations to give a precipitate with ammonium sulfide (difference from manganese and zinc) but it is readily decomposed by an oxidizing agent such as chlorine, bromine, hypochlorite, or hypobromite:

$$2[Ni(CN)_4]^{--} + 4\,OH^- + 9\,BrO^- + H_2O \rightarrow 2\,Ni(OH)_3 + 8\,CNO^- + 9\,Br^-$$

or

$$2\,[Ni(CN)_4]^{--} + 6\,OH^- + 9\,Cl_2 \rightarrow 2\,Ni(OH)_3 + 8\,CNCl\uparrow + 10\,Cl^-$$

In the above reactions, first of all any excess alkali cyanide present is oxidized to cyanate or to CNCl. In the absence of an excess of cyanide ions, the $[Ni(CN)_4]^{--}$ begins to dissociate, $[Ni(CN)_4]^{--} \rightarrow Ni^{++} + 4\ CN^-$, and as fast as the ions are formed, they both become oxidized.

When cobalt ions are treated with an excess of cyanide ions a cobaltocyanide anion, $[Co(CN)_6]^{---}$, is formed which is readily oxidized even by the oxygen of the air to form cobalticyanide ions, $[Co(CN)_6]^{---}$. These anions are so stable that they are not decomposed by treatment with oxidizing agents in alkaline solution and no cobalt is precipitated with $Ni(OH)_3$ by the above treatment. It is possible to detect 0.2 mg of nickel in the presence of 300 mg of cobalt by this reaction.

The test can be applied to the solution obtained by dissolving the sulfides of nickel and cobalt in aqua regia as follows: Evaporate the solution nearly to dryness to expel most of the acid; add about 5 ml of water and then sodium hydroxide solution, drop by drop, until the solution is neutral or until a permanent precipitate is produced. Add potassium cyanide solution, a few drops at a time, until all or nearly all of any precipitated cyanide redissolves. Then add 0.5 to 3 ml more of potassium cyanide solution according to the probable amount of nickel and cobalt present. Heat to 50° or 60° in an open dish for five minutes, or longer if the solution has not become light colored. This serves to oxidize the cobaltocyanide to cobalticyanide. Filter off and reject any small precipitate that may remain. Add about 3 ml of 2 *N* sodium hydroxide solution and conduct chlorine into the solution in the cold or add a little bromine water. A precipitate of $Ni(OH)_3$ should form within five minutes.

16. **Potassium** and **Sodium Carbonates** precipitate apple-green nickel carbonate:

$$Ni^{++} + CO_3^{--} \rightarrow NiCO_3$$

17. **Potassium Ferricyanide** precipitates yellowish brown nickelous ferricyanide, $Ni_3[Fe(CN)_6]_2$. The precipitate is difficultly soluble in hydrochloric acid. In the presence of tartaric acid and a large excess of ammonia, potassium ferricyanide forms a clear, brownish yellow solution.

18. **Potassium Ferrocyanide** precipitates greenish nickelous ferrocyanide, $Ni_2[Fe(CN)_6]$, which is not very soluble in dilute hydrochloric acid.

19. **Potassium Nitrite** produces in dilute nickel solutions no precipitate (difference from cobalt). In very concentrated solutions a

brownish red precipitate of $Ni(NO_2)_2 \cdot 4\ KNO_2$ is thrown down; in the presence of alkaline earth salts a yellow crystalline precipitate is formed, *e.g.*, $Ni(NO_2)_2 \cdot Ba(NO_2)_2 \cdot 2\ KNO_2$, which is very difficultly soluble in cold water, but readily soluble in boiling water, with a green color.

20. **Potassium Thiocarbonate,** K_2CS_3, gives a dark brown coloration in a concentrated, ammoniacal solution of a nickel salt, or a reddish yellow color if the solution is dilute. This is a sensitive test for nickel; cobalt ions do not interfere, but manganese and zinc ions are likely to interfere.

21. **Sodium Hypochlorite** precipitates in the presence of alkali hydroxide all the nickel as brownish black nickel dioxide, NiO_2. Nickelous hydroxide is first formed by the alkali present, but is is then oxidized by the hypochlorite:

$$Ni^{++} + 2\ OH^- + ClO^- + \rightarrow NiO_2 + Cl^-\ H_2O$$

On adding chlorine or bromine to the nickel solution to which alkali has been added, nickeldioxide is likewise formed:

$$Ni(OH)_2 + 2\ OH^- + Cl_2 \rightarrow 2\ Cl^- + NiO_2 + 2H_2O$$

22. **Sodium Phosphate** precipitates apple-green nickel phosphate,

$$3\ Ni^{++} + 4\ HPO_4^{--} \rightarrow 2\ H_2PO_4^- + Ni_3(PO_4)_2$$

readily soluble in acids, even acetic acid.

Reactions in the Dry Way

The borax and sodium metaphosphate beads are brown in the oxidizing flame, almost the same shade as the strongly saturated manganese bead; in the reducing flame the bead becomes gray, because of the formation of some metallic nickel. On looking at the bead through the microscope the finely divided metal can be seen suspended in the colorless glass.

On heating nickel salts with sodium carbonate on charcoal, a gray scale of metallic nickel is obtained. This reaction is best performed with the charcoal stick, as described on p. 75. The magnetic metal obtained in this way is placed on a piece of filter paper and dissolved in nitric acid, a drop of concentrated hydrochloric acid is added, and the paper is carefully dried by moving it back and forth over the flame. If nickel is present the paper appears greenish (colorless with very small amounts of nickel), or bluish if cobalt is also present. The spot is now moistened with caustic soda or potash, and is then held in bromine vapors, which are obtained by shaking some bromine water in a wide-

mouthed flask. If nickel or cobalt is present, a black spot will be formed by the above treatment, consisting of the hydroxide of the trivalent metal (p. 237). The blackening often does not appear at first; in this case the paper is moistened once more with potassium hydroxide and again treated with bromine. The spot will now appear if nickel is present.

COBALT, Co. At. Wt. 58.94, At. No. 27

Density 8.8. M. P. 1480°. B. P. 2900°

Occurrence. — Like nickel, native cobalt is found only in meteorites. It occurs in the earth's crust chiefly as sulfide, as arsenide, and as salts of thioarsenious and thioantimonous acids; it is almost always accompanied by nickel and iron. The most important ores are smaltite, $CoAs_2$, isometric; cobaltite, CoAsS, isometric; skutterudite, $CoAs_3$, isometric; and erythrite, $Co_3(AsO_4)_2 \cdot 8\ H_2O$, monoclinic, isomorphous with vivianite, $Fe_3(PO_4)_2 \cdot 8\ H_2O$, and with annabergite, $Ni_3(AsO_4)_2 \cdot 8\ H_2O$.

Properties. — Cobalt, from the Greek word *kobalos* = gnome, owes its name to mining superstition concerning imaginary work done by gnomes in the mountains among the ores. The metal, first obtained by Brandt in 1735, is steel gray and resembles iron in appearance, but it is stronger than either iron or nickel. Finely divided cobalt oxidizes readily in moist air. At a white heat it burns to Co_3O_4. It is magnetic but loses this property above 115°. Important alloys of cobalt are stellite, an alloy steel containing cobalt and chromium which is very hard and resists corrosion; carboloy, a tungsten carbide containing cobalt which is very hard; and magnet steel, containing 35 per cent of cobalt. Cobalt oxide is used for imparting a blue color to glass and enamels. The total amount of cobalt produced in a year is estimated to be about 800 tons, which is small compared to the annual production of 53,000 tons of nickel and 60,000,000 tons of steel in the United States alone. The metal dissolves slowly in hot, dilute hydrochloric or sulfuric acid and more rapidly in hot, dilute nitric acid.

Cobalt forms three oxides. Gray to greenish cobaltous oxide, CoO, is obtained by careful heating of the hydroxide or carbonate or by heating other oxides of cobalt in hydrogen; cobaltic oxide, Co_2O_3, is black and can be obtained by heating cobaltous nitrate to about 180°; black cobaltous-cobaltic oxide, Co_3O_4, is the most stable oxide of cobalt and can be prepared by heating the oxides, hydroxides, carbonate, or oxalate of cobalt to redness.

By dissolving these three oxides in acids, salts derived from cobaltous oxide are always obtained, containing bivalent cobalt:

$$CoO + 2\ HCl \rightarrow H_2O + CoCl_2$$
$$Co_2O_3 + 6\ HCl \rightarrow 3\ H_2O + 2\ CoCl_2 + Cl_2\uparrow$$
$$Co_3O_4 + 8\ HCl \rightarrow 4\ H_2O + 3\ CoCl_2 + Cl_2\uparrow$$

Simple cobaltic salts are unknown, but the hydroxide and many complex compounds exist with trivalent cobalt, as, for example, potassium cobaltinitrite, potassium cobalticyanide, and numerous cobaltiammines.

Cobaltous compounds in a crystallized state (as well as in aqueous solution) are pink, in the anhydrous condition blue, yellow, or green, and blue in aqueous solutions in the presence of hydrochloric acid. The solubility reactions of cobaltous salts are similar to those of manganese and nickel.

Reactions in the Wet Way

1. **Alkali Hydroxide** precipitates in the cold a blue basic salt:

$$Co^{++} + Cl^- + OH^- \rightarrow Co(OH)Cl$$

which on warming is further decomposed by hydroxide ions forming pink cobaltous hydroxide:

$$Co(OH)Cl + OH^- \rightarrow Cl^- + Co(OH)_2$$

In a moderately concentrated solution of the alkali hydroxide the precipitate of pink cobaltous hydroxide is sometimes produced in the cold, only after standing some time. The rapidity of the reaction depends entirely upon the concentration of the alkali hydroxide.

Cobaltous hydroxide gradually turns brown in contact with the air, going over into cobaltic hydroxide:

$$4\ Co(OH)_2 + 2\ H_2O + O_2 \rightarrow 4\ Co(OH)_3$$

In this respect cobalt behaves similarly to iron and manganese, and differs from nickel, for the hydroxide of nickel is not oxidized by atmospheric oxygen.

On adding chlorine, bromine, hypochlorites, hydrogen peroxide, etc., to an alkaline solution containing cobaltous hydroxide, cobaltic hydroxide is immediately formed, as with nickel and manganese:

$$2\ Co(OH)_2 + 2\ OH^- + Cl_2 \rightarrow 2\ Cl^- + 2\ Co(OH)_3$$
$$2\ Co(OH)_2 + HOH + OCl^- \rightarrow Cl^- + 2\ Co(OH)_3$$

From ammoniacal cobalt solutions the above oxidizing agents cause no precipitation, but merely a red coloration; the addition of potassium hydroxide then causes no precipitation (difference from nickel).

The presence of non-volatile organic acids or of sugar prevents the precipitation of cobaltous and cobaltic hydroxides.

Cobaltous hydroxide, $Co(OH)_3$, behaves under some conditions as a weak acid, for on adding to a cobaltous solution a very concentrated solution of KOH or NaOH the precipitate at first produced dissolves with a blue color* similar to copper. By the addition of Rochelle salts to this blue cobalt solution the color either disappears almost entirely or becomes a pale pink, while the similarly treated copper solution becomes more intensely blue. By the addition of potassium cyanide to the blue cobalt solution it becomes yellow, and in contact with air turns intensely brown. A copper solution would be decolorized by the addition of potassium cyanide.

By pouring a little cobalt solution (or adding a little solid cobalt carbonate) into a concentrated solution of caustic soda or potash, to which a little glycerol has been added, a blue solution is formed (the color being intensified by warming), and after standing some time in the air, or immediately upon the addition of hydrogen peroxide, it becomes a beautiful green.

2. **Alkali Carbonates** produce a reddish precipitate of basic salt of varying composition.

3. **Ammonia,** in the absence of ammonium salts, precipitates a blue basic salt, soluble, however, in excess of ammonium chloride,

* Ed. Donath, *Z. anal. Chem.*, **40**, 137 (1901).

No precipitate is formed, therefore, in solutions which contain sufficient ammonium chloride, but the dirty-yellow, ammoniacal solution gradually turns reddish on exposure to the air, owing to the formation of very stable cobaltiammines. The bivalent ammines are not very stable.

4. **Ammonium Carbonate** also precipitates a reddish basic salt, soluble, however, in excess.

5. **Ammonium Sulfide** precipitates black cobalt sulfide,

$$Co^{++} + S^{--} \rightarrow \mathbf{CoS}$$

insoluble in ammonium sulfide, acetic acid, and very dilute hydrochloric acid (cf. p. 232); soluble in concentrated nitric acid and aqua regia, with separation of sulfur:

$$3\,\mathbf{CoS} + 8\,HNO_3 \rightarrow 4\,H_2O + 2\,NO\uparrow + 3\,S + 3\,Co(NO_3)_2$$

By continued action of strong nitric acid all the sulfur goes into solution as sulfuric acid.

The addition of an oxidizing agent always helps an acid to dissolve an insoluble sulfide. The solution in contact with a sulfide precipitate at first contains enough sulfide ions to satisfy the solubility product of the sulfide. When hydrogen ions are added nonionized hydrogen sulfide is formed unless the solubility product of the sulfide is so small that less sulfide ions are present than would be formed by the ionization of H_2S. If an appreciable quantity of H_2S is formed, it can be expelled as a gas and the sulfide will dissolve. Sometimes, however, this takes place very slowly and then the addition of an oxidizing agent is necessary. The sulfide ions in solution are oxidized to free sulfur. The solubility product of the sulfide is no longer reached in solution, for as fast as a little of the substance dissolves the sulfide ions are oxidized.

6. **Ammonium Thioacetate** precipitates cobaltous sulfide from ammoniacal solutions. Sodium thiosulfate has no action upon acid solutions, and in neutral solutions an incomplete precipitation of cobaltous sulfide is obtained.

7. **Ammonium Thiocyanate** (Vogel's reaction).* If a concentrated solution of ammonium thiocyanate is added to a cobaltous solution, the latter becomes a beautiful blue, owing to the formation of ammonium cobaltothiocyanate:

$$Co^{++} + 4\,CNS^- + 2\,NH_4^+ \rightarrow (NH_4)_2[Co(CNS)_4]$$

On adding water the blue color disappears and the pink color of the cobaltous salt takes its place. If amyl alcohol† (or a mixture of equal

* *Ber.*, **12**, 2314; Treadwell, *Z. anorg. Chem.*, **26**, 105 (1901).

† T. T. Morrell first showed that cobalt salts give a blue color with ammonium thiocyanate, disappearing on the addition of water, but reappearing when alcohol is added. *Z. anal. Chem.*, **16**, 251.

parts amyl alcohol and ether) is added and the solution shaken, the upper alcoholic layer is colored blue. This reaction is so sensitive that the blue color is recognizable when the solution contains only 0.0002 mg of cobalt. The blue solution also shows a characteristic absorption spectrum.* Nickel salts produce no coloration of the amyl alcohol. If, however, iron is present, red $Fe(CNS)_3$ is formed, which likewise colors the amyl alcohol, making the blue color (due to the cobalt) very indistinct, so that, under some conditions, it can no longer be detected. If, however, 2 or 3 ml of concentrated ammonium acetate solution and 2 or 3 drops of 50 per cent tartaric acid solution are added, the red color produced by $Fe(CNS)_3$ will disappear and the blue color of the cobalt compound will be seen.

The blue color is probably that of undissociated $(NH_4)_2[Co(CNS)_4]$. When the solution is diluted, the salt is ionized and the complex anion also is in equilibrium with cobalt ions; alcohol and ether probably dissolve only the undissociated $(NH_4)_2[Co(CNS)_4]$ which is evidently present to some extent in the aqueous solution. Kolthoff recommends the use of a saturated solution of NH_4CNS in acetone. On the spot plate 1 drop of solution and 5 drops of the acetone reagent will give the test with 0.5 γ of Co^{++}.

8. **Barium Carbonate** precipitates no cobalt in the cold and out of contact with air, but on exposure to the air cobaltic hydroxide is gradually thrown down. The precipitation takes place much more quickly on the addition of hypochlorites or hydrogen peroxide:

$$2\,Co^{++}+2\,BaCO_3+3\,H_2O+OCl^-\rightarrow 2\,Ba^{++}+Cl^-+2\,Co(OH)_3+2\,CO_2\uparrow$$

If the solution is heated to boiling, all the cobalt is precipitated as a basic salt, even out of contact with the air.

9. **Dicyandiamidine Sulfate** gives no precipitate in ammoniacal cobalt solutions upon the addition of sodium hydroxide. If a sufficient quantity of cane sugar is added a complex ion of deep red color is formed with the sugar and there is no danger of precipitating cobalt hydroxide with the sodium hydroxide. This red color can be seen after the precipitation of nickel with dicyandiamidine sulfate.

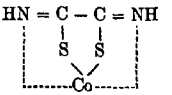
10. **Dimethylglyoxime** gives no precipitate with an ammoniacal cobalt solution, but a wine-red color is obtained if hydrogen sulfide or ammonium sulfide is also present.

11. **Ether Saturated with Hydrogen Chloride** does not precipitate an anhydrous cobaltous salt, as in the case of nickel, but will dissolve the blue anhydrous cobaltous chloride. This furnishes the basis of a method for separating nickel and cobalt.

12. **Hydrogen Sulfide** produces no precipitate in solutions containing mineral acids. In neutral solutions containing an alkali acetate all the cobalt is precipitated as black sulfide.

* Wolff, *Z. anal. Chem.*, **18**, 58.

13. **Hydrorubianic Acid** gives with cobalt, in the presence of ammonia or considerable alkali acetate, a yellowish brown precipitate of



The test succeeds when nickel (cf. p. 235) and copper (cf. p. 135) are absent and 0.03 γ or more of cobalt is present.

Place a drop of the solution on filter paper, hold in the fumes from a bottle of strong ammonia water, and then add 1 drop of a 1 per cent solution of hydrorubianic acid.

14. **α-Nitroso-β-naphthol,** $C_{10}H_6(NO)OH$, produces a voluminous, purple-red precipitate of cobalti-nitroso-β-naphthol, $[C_{10}H_6(NO)O]_3Co$, which is insoluble in cold dilute nitric or hydrochloric acid.*

This reagent not only serves for qualitative purposes, but can also be used for the determination of cobalt in the presence of nickel. The test may be applied conveniently to the solution obtained in the usual qualitative scheme after the removal of all metals except nickel and cobalt. A part of the solution may be used for the sensitive nickel test with dimethylglyoxime (p. 233) and the remainder for the cobalt test.

Dilute the solution to about 50 ml, add 4 ml of 6 *N* hydrochloric acid and 20 ml of 6 *N* acetic acid. Heat, add 50 ml of a saturated solution of α-nitroso-β-naphthol in 50 per cent acetic acid and boil. If as much as 0.1 mg of cobalt is present, a red precipitate or turbidity is obtained even in the presence of 250 mg of nickel. When more than 150 mg of nickel is present, however, some of the brownish yellow nickel compound, $[C_{10}H_6(NO)O]_2Ni$, will precipitate after the solution cools.

The reagent used in this test should be freshly prepared. α-Nitroso-β-naphthol gradually decomposes on standing in the air and changes from yellow to brown or even black in color. It can be purified by dissolving in hot sodium carbonate, filtering, and reprecipitating with sulfuric acid. For all ordinary purposes the saturated solution in 50 per cent acetic acid is suitable. The cobalt test can be made more delicate by adding an equal volume of alcohol to the test, and for detecting traces of cobalt, an aqueous solution of the organic substance can be used, but since 5000 ml of water are required to dissolve 1 g of the α-nitroso-β-naphthol, it is evident that the aqueous solution is not suitable when much cobalt is present. An excess of the reagent is required, as a part of it is used to oxidize the cobalt to the trivalent condition.

Copper gives a characteristic coffee-brown precipitate with the reagent, and it is possible to separate copper from lead, cadmium, etc., by means of it. Ferric iron gives a brownish black precipitate which is insoluble enough to serve as a means of separating iron from aluminum, manganese, etc. Ferrous iron also gives a greenish precipitate in neutral solution. Of all these precipitates, however, the cobalt compound is the most characteristic and the least influenced by the presence of acid. Thus, with the acidity recommended above, the presence of a little ferric or ferrous iron causes no disturbance.

* Ilinski and v. Knorre, *Ber.*, **18**, 699 (1885).

F. W. Atack* prepares the reagent by dissolving 0.1 g of α-nitroso-β-naphthol in 20 ml of water and 1 ml of dilute sodium hydroxide, filtering the hot solution and diluting to 200 ml. With this reagent, W. Böttger† has detected as little as 0.006 γ of cobalt in 0.01 ml of solution. Place 1 drop of the solution to be tested on filter paper. If much acid is present, hold over the neck of the strong ammonia bottle. Add 1 drop of the nitrosonaphthol reagent and finally 1 drop of 2 N H_2SO_4.

15. **Potassium Chromate** gives a brownish red precipitate of basic cobaltous chromate, $CoCrO_4 \cdot CoO \cdot H_2O$. The precipitate dissolves in acids and in ammonia water.

16. **Potassium Cyanide** produces in neutral solutions a reddish brown precipitate, soluble in excess of potassium cyanide in the cold, with a brown color, forming potassium cobaltocyanide:

$$Co^{++} + 2\,CN^- \rightarrow Co(CN)_2;\ Co(CN_2) + 4\,CN^- \rightarrow [Co(CN)_6]^{----}$$

On warming the brown solution for some time it becomes bright yellow and reacts alkaline; it now contains potassium cobalticyanide, analogous in composition to potassium ferricyanide. The formation of the cobaltic salt takes place with the help of atmospheric oxygen:

$$4\,[Co(CN)_6]^{----} + O_2 + 2\,H_2O \rightarrow 4\,[Co(CN)_6]^{---} + 4\,OH^-$$

The reaction takes place more quickly in the presence of chlorine, bromine, hypochlorites, etc.:

$$2\,[Co(CN)_6]^{----} + Cl_2 \rightarrow 2\,[Co(CN)_6]^{---} + 2\,Cl^-$$

An excess of chlorine, bromine, etc., does not decompose the cobaltic salt (difference from nickel).

The cobalticyanide anion is much more stable than the cobaltocyanide anion. By adding hydrochloric acid to the brown solution of potassium cobaltocyanide, hydrogen cyanide will be set free and yellow cobaltous cyanide formed,

$$[Co(CN)_6]^{----} + 4\,H^+ \rightarrow 4\,HCN + Co(CN)_2$$

while potassium cobalticyanide is not decomposed by hydrochloric acid.

If potassium nitrite and acetic acid are added to a solution of potassium cobaltocyanide, the liquid becomes blood-red in color owing to the formation of potassium nitrocobalticyanide, $K_4Co_2(CN)_9NO_2 \cdot 3\,H_2O$.

If a solution of potassium cobaltocyanide is shaken with sodium hydroxide, it becomes brown and on adding yellow ammonium sulfide a blood-red coloration is obtained.

Potassium cobalticyanide forms, with most of the heavy metals, difficultly soluble or insoluble salts possessing characteristic colors. Thus, it produces with cobaltous salts pink cobaltous cobalticyanide:

$$2\,[Co(CN)_6]^{---} + 3\,Co^{++} \rightarrow Co_3[Co(CN)_6]_2$$

and with nickel salts greenish nickelous cobalticyanide.

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* *J. Soc. Chem. Ind. Japan*, **34**, 641 (1915).

† *Mikrochemie, Emich Festschrift*, **1930**, 28.

If, therefore, a cobalt solution contains nickel it gives, on precipitating and redissolving with potassium cyanide, boiling, and adding hydrochloric acid, a greenish precipitate of nickelous cobalticyanide:

$$2\,[Co(CN)_6]^{---} + 3\,[Ni(CN)_4]^{--} + 12\,H^+ \rightarrow 12\,HCN + Ni_3[Co(CN)_6]_2$$

17. **Potassium Ferricyanide** precipitates brownish red cobaltous ferricyanide, $Co_3[Fe(CN)_6]_2$, scarcely soluble at all in hydrochloric acid. If tartaric acid or ammonium chloride and an excess of ammonia are added to a solution of a simple cobalt salt, a clear solution is obtained; the addition of ferricyanide causes a yellowish red coloration. This sensitive reaction has been recommended for the detection of cobalt in the presence of nickel.

18. **Potassium Ferrocyanide,** precipitates green cobaltous ferrocyanide, $Co_2[Fe(CN)_6]$, difficultly soluble in hydrochloric acid.

19. **Potassium Nitrite** produces in concentrated solutions of cobalt salts, with the addition of acetic acid, an immediate precipitation of yellow, crystalline potassium cobaltinitrite.

$$Co^{++} + 7\,NO_2^- + 3\,K^+ + 2\,H^+ \rightarrow NO + H_2O + K_3[Co(NO_2)_6]$$

If the solution is dilute, the precipitate appears only after standing for some time, but more quickly on rubbing the sides of the beaker. This reaction offers an excellent means for detecting the presence of cobalt in nickel salts.

20. **Potassium Thiocarbonate,** K_2CS_3, added to an ammoniacal cobalt solution, gives a brownish or black color if much cobalt is present, and a wine-yellow color with very little cobalt.

DETECTION OF TRACES OF COBALT IN NICKEL SALTS

To test a nickel salt for cobalt, add a concentrated solution of ammonium thiocyanate to the solution of a considerable amount of the salt, a few milliliters of amyl alcohol and ether, and shake the mixture. After settling, if the upper alcohol-ether layer is colorless, then the nickel salt contains neither iron nor cobalt; if the layer is reddish, iron is present. In the latter case add 2 or 3 ml of concentrated ammonium acetate solution and 2 or 3 drops of 50 per cent tartaric acid solution and shake again; if cobalt is present the alcohol-ether layer is now distinctly blue.

Sometimes when very little cobalt and considerable nickel are present it is difficult to tell whether the amyl alcohol is colored blue or not. In that event pour the solution into a separatory funnel and draw off the lower layer consisting of the green nickelous solution. Add a little more ammonium thiocyanate solution to the amyl

alcohol, 1 ml of ammonium acetate solution, 1 drop of tartaric acid solution and shake again. The blue color should now appear if any cobalt is present.

Reactions in the Dry Way

The bead produced by borax or sodium metaphosphate is blue in both the oxidizing and reducing flames. By holding the bead in the upper reducing flame for a long time it is possible to reduce the cobalt to metal, when it appears, like nickel, gray.

On the charcoal stick cobalt compounds yield gray metallic cobalt, which can be removed by means of a magnetized knife-blade, placed on filter paper, dissolved in hydrochloric acid and dried, as described on page 76. The paper is then colored blue by cobalt (difference from nickel). If, now, sodium hydroxide is added and the paper exposed to the action of bromine vapors, black cobaltic hydroxide, $Co(OH)_3$, is formed.

ZINC, Zn. At. Wt. 65.38, At. No. 30

Density 7.14. M. P. 419°. B. P. 918°

Occurrence. — Smithsonite, $ZnCO_3$, isomorphous with calcite, $CaCO_3$, etc.; sphalerite, ZnS, isometric; calamine, $Zn_2SiO_4 \cdot H_2O$, orthorhombic, hemimorphic; zincite, ZnO, hexagonal; and franklinite, $(FeO_2)_2(Fe,Mn,Zn)$, isometric. The most important zinc ore is sphalerite, ZnS. Sulfide of zinc is dimorphic and is also found as wurtzite, which crystallizes in the hexagonal system.

Properties. — Metallic zinc is bluish white. At low temperatures and at about 200° C it is so brittle that it can be pulverized, but at 110°–150° C it is ductile and can be drawn out into wire and rolled into foil. The metal was first obtained by Homberg in 1695, and it owes its name to the German word *Zink*. About 1,500,000 metric tons are produced annually. It is used as a protective coating for iron (galvanized iron), as a constituent of brass, as the negative element in dry cells, and, as oxide, in white paint. It forms only one oxide, ZnO, which can be prepared by heating in the air zinc itself or its hydroxide, carbonate, nitrate, oxalate, sulfide, or any of its organic compounds.

Zinc, as its position in the electromotive series indicates (p. 43), dissolves readily in all acids; in hydrochloric,* sulfuric, and acetic acids with evolution of hydrogen:

$$Zn + 2\,H^+ \rightarrow Zn^{++} + H_2\uparrow$$

Zinc is such a strong reducing agent that it easily reduces nitric acid, the extent of the reduction depending upon the concentration of the acid. With very concentrated acid, some NO_2 is obtained, while dilute acid is reduced to ammonium nitrate. In ordinary acid the principal product is nitric oxide, NO:

$$3\,Zn + 8\,HNO_3 \rightarrow 3\,Zn^{++} + 6\,NO_3^- + 4\,H_2O + 2\,NO\uparrow$$
$$4\,Zn + 10\,HNO_3 \rightarrow 4\,Zn^{++} + 8\,NO_3^- + NH_4NO_3 + 3\,H_2O$$

Concentrated nitric acid does not dissolve zinc readily because zinc nitrate is not very soluble in strong nitric acid.

* Absolutely pure zinc dissolves very slowly in these acids, but the metal dissolves readily if a trace of some metal lower in the electromotive series is present.

Like aluminum, zinc dissolves in caustic soda or potash, with evolution of hydrogen and the formation of a zincate:

$$Zn + 2\ OH^- \rightarrow ZnO_2^{--} + H_2\uparrow$$

Zinc oxide, ZnO, is a white infusible powder, which becomes yellow when heated, but turns white again on cooling. Zinc oxide dissolves readily in acids, forming zinc salts:

$$ZnO + 2\ H^+ \rightarrow Zn^{++} + H_2O$$

and in alkali hydroxides forming zincates, *e.g.*, Na_2ZnO_2:

$$ZnO + 2\ OH^- \rightarrow ZnO_2^{--} + H_2O$$

There exists only one series of zinc salts, and the zinc is always bivalent. Most of the salts are white. The chloride, nitrate, sulfate, and acetate are soluble in water; the remainder dissolve readily in mineral acids.

Reactions in the Wet Way

1. **Alkali Hydroxides** precipitate white, gelatinous zinc hydroxide, easily soluble in excess of the precipitant, forming a zincate:*

$$Zn^{++} + 2\ OH^- \rightarrow Zn(OH)_2;\ Zn(OH)_2 + OH^- \rightleftarrows HZnO_2^- + H_2O$$

Zinc hydroxide, like aluminum hydroxide, is amphoteric and behaves sometimes as a base and sometimes as an acid.

On boiling a dilute solution of a zincate, hydrolysis takes place and zinc hydroxide is precipitated, but if the solution contains an excess of OH^- ions, there is no precipitation.

2. **Alkali Carbonates** precipitate a white basic carbonate, of variable composition, as with magnesium.

3. **Alkali Phosphate** precipitates gelatinous, tertiary zinc phosphate, which soon becomes crystalline, and is soluble in ammonia and in acids:

$$3\ Zn^{++} + 4\ HPO_4^{--} \rightarrow 2\ H_2PO_4^- + Zn_3(PO_4)_2$$

In the presence of ammonium salt, the less soluble zinc ammonium phosphate is precipitated:

$$Zn^{++} + NH_4^+ + 2\ HPO_4^{--} \rightarrow H_2PO_4^- + ZnNH_4PO_4$$

Both zinc phosphate and zinc ammonium phosphate dissolve readily in dilute acids, owing to the formation of very slightly ionized HPO_4^{--}, and in dilute ammonia, owing to the formation of zinc ammonia cations. Acids, therefore, deprive the solution of PO_4^{---} anions by forming

* According to Hantzsch the zinc is not present as zincate, but probably in colloidal solution. *Z. anorg. Chem.*, **30**, 289 (1902). In fairly concentrated solutions, however, it is certain that the zinc is present as zincate, for F. Foerster and O. Günther, *Z. Electrochem.*, **6**, 301 (1900), have isolated the compound, $NaHZnO_2 \cdot 3\ H_2O$, as needles with silky luster.

HPO_4^{--}, and ammonia deprives the solution of zinc ions by forming $[Zn(NH_3)_6]^{++}$.

4. **Ammonia** precipitates from neutral solutions, free from ammonium salts, zinc hydroxide, readily soluble in ammonium salts, as in the case of magnesium, nickel, manganese, or iron:

$$Zn^{++} + 2\ NH_3 + 2\ H_2O \rightleftarrows \mathbf{Zn(OH)_2} + 2\ NH_4^+$$

Zinc hydroxide is also soluble in an excess of ammonia, owing to the formation of complex zinc ammonia ions:

$$\mathbf{Zn(OH)_2} + 6\ NH_3 \rightarrow [Zn(NH_3)_6]^{++} + 2\ OH^-$$

5. **Ammonium Carbonate** may precipitate a basic carbonate but the precipitate is soluble in an excess of the reagent. The presence of ammonium salts or of ammonia prevents the precipitation.

6. **Ammonium Sulfide** precipitates from neutral, alkaline or faintly acid solutions all the zinc as amorphous sulfide:

$$Zn^{++} + S^{--} \rightarrow \mathbf{ZnS}$$

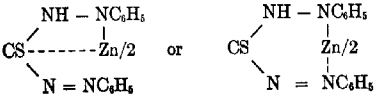
Zinc sulfide is a precipitate difficult to filter; it runs through the filter paper, particularly on washing. This is a peculiarity of almost all metallic sulfides and of many other amorphous bodies, such as aluminum hydroxide, titanic acid, tungstic acid, and many others, and is due to their tendency to form colloidal solutions (p. 64). The colloid can be precipitated by adding a concentrated salt solution or by boiling.

In order, then, to obtain zinc sulfide in a form which can be filtered, it is best precipitated from a boiling solution containing acetic acid and a considerable quantity of ammonium salts. The precipitate may be washed with a solution of ammonium chloride to which a little ammonium sulfide has been added.

7. **Ammonium Thioacetate** precipitates ZnS from ammonia calsolutions but not from acid solutions. Sodium thiosulfate has no effect.

8. **Barium Carbonate** precipitates no zinc in the cold, but on boiling all the zinc is precipitated as basic carbonate.

9. **Diphenylthiocarbazone,** ***dithizone,*** $C_6H_5N : N \cdot SC \cdot NH \cdot NHC_6H_5$, gives in neutral, basic, or acetate solutions a purple-red zinc salt which is soluble in CCl_4. Dissolve 2 mg of the organic substance in 100 ml of CCl_4 and add 1 drop of this reagent to 1 drop of the solution to be tested in a small test tube. On shaking, the green color of the reagent will turn to red if 0.9 γ of zinc is present (H. Fischer, Feigl). The salt formed is usually formulated (cf. p. 135):



The test is not specific since many other ions react with dithizone to give colored products. Feigl recommends the following procedure for carrying out the test in an alkaline solution:

Place 1 drop of the solution to be tested on a watch glass; add 1 drop of 2 *N* sodium hydroxide solution and a few drops of a solution of 0.01 g dithizone in 100 ml of carbon tetrachloride. Allow to evaporate somewhat and blow away the vapors of CCl_4. A red solution will be obtained if 5 γ of zinc is present.

10. Hydrogen Sulfide precipitates the zinc as sulfide, from neutral solutions of a zinc salt:

$$Zn^{++} + H_2S \rightleftarrows ZnS + 2\ H^+$$

The solubility product of zinc sulfide (p. 23) is about 1.2×10^{-23}. At 25° the concentration of a saturated solution of hydrogen sulfide is about 0.1 molar, and the ionization constant for the complete ionization, $H_2S \rightleftarrows 2\ H^+ + S^{--}$, has been estimated to be 1.1×10^{-23}. The concentration of the sulfide ion in such a solution is approximately 1.2×10^{-15} molar equivalent per liter. The solubility product of zinc sulfide is evidently exceeded when the aqueous solution of a zinc salt is saturated with hydrogen sulfide and zinc sulfide is precipitated. The mass-action principle applied to the complete ionization of hydrogen sulfide shows that the concentration of sulfur ions is inversely proportional to the square of the concentration of the hydrogen ions. If the concentration of the hydrogen ions is increased one thousandfold, and this is approximately the case when the solution is tenth-normal with a mineral acid, the concentration of the sulfide ions from hydrogen sulfide is reduced to one-millionth of its value in pure water.

The separation of the second group of metals from the third group is usually accomplished by passing hydrogen sulfide into a solution which is about 0.3-normal with hydrochloric or nitric acid. The concentration of the sulfide ion when such a solution is saturated with hydrogen sulfide at 25° is about 1.1×10^{-22}. To reach the solubility product of zinc sulfide in 0.3-normal acid, the zinc ions should reach the concentration of about 0.11 mole per liter, or about 0.7 g per 100 ml.* If the zinc salt has a greater concentration than this, some zinc sulfide may be precipitated by hydrogen sulfide in 0.3-normal acid solution. The precipitation would evidently be incomplete, for, as more hydrogen ions are formed in solution from the hydrogen sulfide as a result of the sulfide precipitation, the ionization of the hydrogen sulfide continually tends to become less.

If, however, considerable sodium or ammonium acetate is added to the acid solution, the concentration of the hydrogen ion becomes much smaller and the ionization of the hydrogen sulfide takes place to a greater extent. It is then possible to precipitate the zinc as sulfide so completely that less than 1 mg of zinc will remain in solution.

Zinc sulfide dissolves readily in normal hydrochloric acid. The sulfur ions from the zinc sulfide enter into equilibrium with the hydrogen ions of the acid to form hydrogen sulfide. In normal acid solution, the concentration of sulfur ions from saturated hydrogen sulfide is about 1.2×10^{-23} and of sulfur ions from a saturated solution of ZnS in water about 3.5×10^{-12}.

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* This value is merely an approximation, being derived by a rough calculation from values which are not absolutely certain.

11. **Potassium Cyanide** produces a white precipitate of zinc cyanide, soluble in an excess of the precipitant:

$$Zn^{++} + 2\ CN^- \rightleftarrows \mathbf{Zn(CN)_2};\ Zn(\mathbf{CN})_2 + 2\ CN^- \rightarrow [Zn(CN)_4]^{--}$$

The zinc-cyanide anion is decomposed by acids and by alkali sulfide:

$$[Zn(CN)_4]^{--} + 2\ H^+ \rightarrow \mathbf{Zn(CN)_2} + 2\ HCN$$
$$[Zn(CN)_4]^{--} + S^{--} \rightarrow \mathbf{ZnS} + 4\ CN^-$$

12. **Potassium Ferricyanide** precipitates brownish yellow zinc ferricyanide, $Zn_3[Fe(CN)_6]_2$, soluble in hydrochloric acid and in ammonia.

13. **Potassium Ferricyanide** and **Diethylaniline** give a precipitate of zinc ferrocyanide which is colored yellow, brown, or reddish by an oxidation product of diethylaniline.

Potassium ferricyanide can oxidize diethylaniline, as well as other aromatic amines, forming colored organic products and potassium ferrocyanide. The reaction takes place very slowly, but if something is added, such as Zn^{++} which reacts with the $Fe(CN)_6^{----}$ as fast as it is formed, then, in accordance with the mass-action law, the oxidation of the ethylaniline takes place more rapidly. The fact that the reaction does take place rapidly indicates the presence of zinc, provided nothing else is present that reacts with ferrocyanide. The test is suitable for detecting zinc in the presence of aluminum and chromium but cannot be used in the presence of cobalt, nickel, manganese, copper, or much iron. The test can be obtained with less than 1 mg of zinc.

Place 15 drops of 2 per cent potassium ferricyanide solution on a spot plate and mix with 10 drops of a solution of 0.25 g diethylaniline (free from monoethylaniline) in 200 ml of 18 *N* sulfuric acid or of 0.5 g diethylaniline in 200 ml of 50 per cent phosphoric acid. Now add a drop of the solution to be tested, and, if zinc is present, a dark reddish brown or reddish yellow coloration or precipitate will appear within five minutes.

14. **Potassium Ferrocyanide** precipitates white zinc ferrocyanide, which is changed by an excess of the potassium ferrocyanide into less soluble zinc-potassium ferrocyanide:

$$[Fe(CN)_6]^{--} + 2\ Zn^{++} \rightarrow \mathbf{Zn_2[Fe(CN)_6]}$$
$$3\ \mathbf{Zn_2[Fe(CN)_6]} + K_4[Fe(CN)_6] \rightarrow 2\ \mathbf{K_2Zn_3[Fe(CN)_6]_2}$$

By treatment with bromine, the precipitate is changed into a yellow oxidation product.

15. **Potassium Periodate** gives a white precipitate in aqueous solutions. The presence of ammonium chloride tends to prevent the precipitation in the cold but on boiling all the zinc is thrown down.

Reactions in the Dry Way

By heating with sodium carbonate on charcoal before the blowpipe, it is not possible to obtain metallic zinc on account of its volatility; but an incrustation of oxide is obtained which is yellow when hot and white when cold.

Zinc oxide (or such compounds of zinc as are changed over to oxide on ignition), when moistened with cobalt nitrate and ignited, yields a green infusible mass — Rinmann's green. This test is performed as with aluminum (p. 194).

ANALYSIS OF GROUP III

Separation of the Metals of Group III from the Alkalies and Alkaline Earths

The separation of the members of the ammonium sulfide group from the alkalies and alkaline earths is effected by means of ammonium sulfide and ammonium chloride. If, however, the solution contains phosphoric acid, oxalic acid, or considerable boric acid, the neutralization of the solution will cause the precipitation of calcium, strontium, barium, and magnesium as phosphate, oxalate, or borate. Hydrofluoric acid causes precipitation of calcium fluoride in this group.

There are four well-known ways for overcoming the difficulty caused by the presence of phosphoric acid:

1. **The Tin Method.** —When tin is boiled with concentrated nitric acid, insoluble metastannic acid is formed, which has the property of adsorbing H_3PO_4 and H_3AsO_4; if sufficient tin is used, all H_3PO_4 is removed from the solution. The filtrate from Group II, therefore, can be evaporated to a small volume, treated with 10 ml of concentrated HNO_3, again evaporated to make sure that all Cl^- is removed, treated with more HNO_3 and with small portions of pure Sn until a little of the solution fails to give the test for H_3PO_4 with molybdate reagent. This method is good but takes time, and the precipitate is hard to filter.

2. **The Basic Acetate Method.** — This procedure will be given in Table V. It calls for the presence of at least one atom of Fe^{+++} for each mole of PO_4^{---} present, careful neutralization, and boiling with sodium acetate solution. Under these conditions, the PO_4^{---} is precipitated as $FePO_4$ and the excess Fe^{+++} as basic acetate.

3. **The Zirconyl Chloride Method.** — $ZrOCl_2$ will precipitate PO_4^{---} from solutions which are 0.3 *N* in HCl. The excess Zr can be removed from the solution by taking advantage of the fact that, after excess Zr is precipitated as $Zr(OH)_4$ by adding NH_4OH and boiling a few minutes, the precipitate of $ZrH(PO_4)_2$ and $Zr(OH)_4$ is not dissolved easily by dilute HCl.

To carry out this procedure, expel H_2S from the filtrate from Group II, test with NH_4OH, and if a precipitate forms make a portion of the solution distinctly acid with HNO_3, heat nearly to boiling, and test with ammonium molybdate reagent. If the test is positive, add 2 g of NH_4Cl and 10 ml of $ZrOCl_2$ reagent (322 g of $ZrOCl_2 \cdot 8\,H_2O$ per liter) dropwise. Stir vigorously, add 0.2 g of asbestos, make alkaline with NH_4OH, and boil two minutes. Filter hot with gentle suction. Refilter if necessary, and test the filtrate again for H_3PO_4.

4. The fourth method serves to overcome the precipitation of alkaline earths (but not magnesium) as phosphate, oxalate, or fluoride when the solution is neutralized with NH_4OH. Evaporate the solution to dense fumes after adding 5 ml of concentrated H_2SO_4. Cool; add 15 ml of water very carefully and 45 ml of alcohol. This serves to precipitate sulfates of Ba, Ca, and Sr. Filter and examine the filtrate for Groups III and V. Boil the precipitate with 3 *N* Na_2CO_3, filter, repeat the treatment with Na_2CO_3, and wash the precipitate until the washings are practically neutral to litmus. Dissolve the residual carbonates in hot dilute acetic acid and test for Ba, Sr, and Ca in the usual way.

TABLE V. — ANALYSIS OF GROUP III

Solution may contain Fe^{++}, Fe^{+++}, Al^{+++}, Cr^{+++}, Mn^{++}, Zn^{++}, Co^{++}, Ni^{++}, and Groups IV and V.

Add NH_4OH and $(NH_4)_2S$. Filter and examine filtrate for Groups IV and V (p. 275). *Dissolve ppt. in HCl and $KClO_3$. Evaporate, treat with NaOH and Na_2O_2, and filter.* (2)

Precipitate: $Fe(OH)_3$, H_2MnO_3, $Co(OH)_3$, $Ni(OH)_2$, $[Zn(OH)_2]$. *Dissolve in HNO_3 and H_2O_2. Evaporate and boil with conc. HNO_3+$KClO_3$.* (3)

Filtrate: AlO_2^-, CrO_4^{--}, $HZnO_2^-$. *Acidify with HCl and add NH_4OH.* (12)

Precipitate: MnO_2. *Dissolve in HNO_3 + H_2O_2 and test for Mn with $NaBiO_3$.* (4)

Filtrate: Fe^{+++}, Co^{++}, Ni^{++}, $[Zn^{++}]$. *Add NH_4OH.* (5) *If phosphate is present, proceed as outlined in* 6.

Precipitate: $Fe(OH)_3$. *Test for Fe with $K_4Fe(CN)_6$.* (5 or 6)

Filtrate: $Co(NH_3)_6^{++}$, $Ni(NH_3)_6^{++}$, $[Zn(NH_3)_6^{++}]$. *Saturate with H_2S and treat ppt. with cold, normal HCl.* (7)

Residue: CoS, NiS. *Dissolve in HCl and $KClO_3$ and evaporate just to dryness. Add $HC_2H_3O_2$ and KNO_2 to precipitate cobalt as yellow $K_3[Co(NO_2)_6]$. Filter and test the filtrate with dimethylglyoxime.* Red precipitate of $Ni[(CH_3C{=}NO)_2H]_2$ shows the presence of nickel. (8)

Solution: Zn^{++}, traces of Co^{++} and Ni^{++}. *Add NaOH and Na_2O_2.* (9)

Precipitate: $Co(OH)_3$ $Ni(OH)_2$. *Add to residue of CoS, NiS.* (10)

Filtrate: Na_2ZnO_2. *Acidify with $HC_2H_3O_2$ and saturate with H_2S. Confirm Zn by the Rinmann's green test.* (11)

Precipitate: $Al(OH)_3$. *Dissolve in HCl and test with aluminon or dissolve in HNO_3, add $Co(NO_3)_2$ solution, filter and ignite the residue.* A red precipitate with aluminon or the formation of Thénard's blue by ignition shows the presence of aluminum. (13)

Filtrate: $Zn(NH_3)_6^{++}$, CrO_4^{--}. *Boil with Na_2CO_3, till all NH_3 is expelled.* (14)

Precipitate: $Zn(OH)_2CO_3$. *Dissolve in a little HCl, add NH_4OH and $HC_2H_3O_2$ and test with H_2S.* White precipitate: ZnS. (15)

Filtrate: CrO_4^{--}. *Add $HC_2H_3O_2$ and $Pb(C_2H_3O_2)_2$.* Yellow precipitate: $PbCrO_4$. (16)

PROCEDURE

1. Boil a little of the filtrate from Group II until the hydrogen sulfide is expelled, pour the solution into a mixture of 5 ml 6-normal nitric acid and 5 ml of ammonium molybdate reagent, heat to 60°, and allow to stand for ten minutes. If a yellow precipitate of ammonium phosphomolybdate is obtained, members of Group IV are likely to precipitate as phosphates upon the neutralization of the solution by ammonia and ammonium sulfide.

Boil the remainder of the filtrate from Group II until hydrogen sulfide is expelled, and make alkaline with ammonium hydroxide. (No precipitate shows absence of Al, Cr, Fe, and alkaline earth phosphate.) Add ammonium sulfide reagent in small portions until, after shaking the flask and blowing away the vapors, a black coloration is obtained on moist lead acetate paper held near the mouth of the flask. Heat nearly to boiling, shake, and let stand about three minutes. Filter; wash the precipitate with water containing 1 per cent ammonium sulfide and finally with pure water. If the filtration is slow, keep the funnel covered with a watch glass to avoid oxidation of the precipitate. Test the filtrate with a few drops of ammonium sulfide reagent, and heat to see if any dark precipitate forms which should be filtered off through a fresh filter. Use the filtrate for the Group IV tests (p. 275).

2. Digest the precipitate with 5–15 ml of cold, 6-normal hydrochloric acid for a few minutes and afterwards boil for a short time. If there is a black residue, sprinkle a little powdered potassium chlorate into the hot, but not boiling, solution. Then boil for a minute and filter. Reject the residue, which should be sulfur possibly blackened by a little enclosed sulfide. Evaporate the solution nearly to dryness to remove the excess of acid, dilute to about 25 ml, and carefully neutralize with pure sodium hydroxide. If a very heavy precipitate is produced, it is best to dilute with a little more water. To the cold solution carefully add a little sodium peroxide powder. (On account of the violent reaction with water, and the fact that the powder often contains a little free sodium, care should be taken not to add the peroxide too fast or to a hot solution. Only a little peroxide should be taken from the container at one time and it should be transferred directly to glass and never to paper.) Finally boil the solution to decompose the excess of peroxide, dilute with an equal volume of water, and filter. *The precipitate contains ferric hydroxide, hydrated manganese dioxide, cobaltic hydroxide, and nickelous hydroxide. The filtrate contains sodium aluminate, chromate, and zincate.* The separation is faulty in the case of zinc which normally stays in solution. As much as 5 mg of zinc may be carried down with the pre-

cipitate when much iron, nickel, or cobalt is present, and as much as 20 mg by considerable manganese. This is probably due to the amphoteric nature of the precipitated hydroxides and the insolubility of the zinc salts of the corresponding acids. Examine the filtrate for chromium, aluminum, and zinc by § 12.

3. Dissolve the precipitate in hot, 6-normal nitric acid, adding as much hydrogen peroxide as is necessary to reduce the manganese and cobalt to the bivalent condition (cf. p. 35). Evaporate the solution nearly to dryness, add 15 ml of 16-normal nitric acid and about 1 g powdered potassium chlorate, and heat to boiling. Add 10 ml more of concentrated nitric acid, heat to boiling, remove the flame, and add 0.5 g more of potassium chlorate. Repeat the treatment with fresh portions of chlorate until about 3 g of chlorate have been used. Do not add the chlorate to the nitric acid solution while it is boiling, since an explosion is likely to result, but boil after the addition of each portion of chlorate. The treatment with chlorate is best accomplished in a 250-ml Erlenmeyer flask. If a precipitate of MnO_2 is formed, filter through a thin layer of good quality, washed asbestos which is supported by a little glass wool in an ordinary funnel. Test the filtrate for manganese by adding 1 g of potassium chlorate and boiling again. Wash the precipitate with a little concentrated nitric acid, which has been freed from nitrous acid by boiling with a little potassium chlorate just previous to use. Examine the filtrate for iron, cobalt, nickel and zinc, by § 5 or by § 6 if H_3PO_4 is present.

4. Dissolve the precipitated manganese dioxide with a little hot 6-normal nitric acid and a few drops of hydrogen peroxide. Boil to decompose any excess of the latter, and cool to room temperature. Add a little solid sodium bismuthate, shake, and let the solid settle. A purple solution shows the presence of *manganese* (cf. p. 226).

5. If phosphate is absent, pour the cold filtrate from § 3 into a volume of 6-normal ammonium hydroxide which is four times as large as the volume of concentrated nitric acid used in § 3. A dark red precipitate indicates the presence of iron. Filter, and examine the filtrate for nickel, cobalt, and zinc by § 7. Pour a mixture of 2 ml potassium ferrocyanide reagent and 10 drops of 6-normal acetic acid over the precipitate of ferric hydroxide on the filter. A dark blue or green residue on the filter proves that *iron* is present.

6. If a test for phosphoric acid was obtained in § 1, first test for iron as follows: Evaporate one-tenth of the solution from § 3 almost to dryness, heat with 3 ml of 6-normal hydrochloric acid till no more chlorine is evolved, and add 20 ml of water with a little potassium ferrocyanide solution. If iron is present a dark blue color is obtained.

Neutralize the remainder of the nitric acid solution from § 3 with

ammonium hydroxide, adding the reagent until a slight precipitate is formed which does not redissolve by shaking for fifteen seconds. If no precipitate forms, add ammonium hydroxide until alkaline and pass on to § 7. If a precipitate forms, add 50 ml of water and 15 ml of 3-normal ammonium acetate solution. Unless the solution is already reddish in color, add ferric nitrate solution, in portions of 1 ml, until a deep red color is obtained. Boil the mixture gently for three minutes, adding 50 ml more of water if a large precipitate forms. (If the iron does not precipitate but remains in colloidal solution, add 30 drops more of ammonium hydroxide and boil again.) By this treatment any phosphoric acid is precipitated as ferric phosphate and the excess of iron added is precipitated as basic ferric acetate (see p. 213). Filter while still hot and reject the precipitate. Make the filtrate alkaline with ammonium hydroxide, filter if necessary, and treat the filtrate by § 7.

7. Saturate the filtrate from § 5 or § 6 with hydrogen sulfide, filter off the precipitated cobalt, nickel, and zinc sulfides, and reject the filtrate unless phosphate was found present and the procedure described in § 6 was followed. In that case examine the filtrate for barium, calcium, strontium, and magnesium but not for the alkalies, as these have been added (p. 275). Do not, therefore, mix this filtrate with that obtained in the original separation of Group III from Group IV, which must in all cases be examined separately for alkali and alkaline earth cations. Digest the precipitated sulfides with 10–30 ml of cold, normal hydrochloric acid to dissolve any zinc sulfide that may be present; a little nickel and a trace of cobalt may be dissolved by this treatment. Examine the solution for zinc by § 9 and § 11.

8. Test the sulfide residue obtained in § 7 together with the sodium peroxide precipitate obtained in § 9 for nickel and cobalt as follows: Dissolve the precipitate in a casserole by adding 5–15 ml of 6-normal hydrochloric acid, heating to boiling and sprinkling a little potassium chlorate powder into the hot solution. Filter off any sulfur residue and evaporate the solution to dryness, but avoid overheating the residue. Dissolve in 5 ml of 6-normal acetic acid, add 3 ml of 6-normal potassium nitrite reagent, and allow to stand with occasional shaking for at least fifteen minutes. A yellow precipitate of potassium cobaltinitrite proves *cobalt* to be present. If much precipitate forms, add to the mixture 10 ml more of 6-normal potassium nitrite solution and about 3 g of powdered potassium chloride. After standing with frequent shaking for another fifteen minutes, filter and reject the precipitate.

To a part of the filtrate, add 10 ml of water and 4 ml of dimethylglyoxime reagent. Heat to boiling and allow to stand for a few minutes. A red precipitate shows that *nickel* is present.

9. Neutralize the solution obtained in § 7 with sodium hydroxide and add sodium peroxide as in § 2. Examine the filtrate by § 11.

10. If deemed advisable, any precipitated $Ni(OH)_2$ and $Co(OH)_3$ from § 9 may be added to the sulfide residue obtained in § 7 and tested for nickel and cobalt as in § 8.

11. Acidify the filtrate from § 9 with acetic acid and saturate the solution with hydrogen sulfide. Any white precipitate that forms is probably zinc sulfide. Filter off the precipitate and dissolve it in 5–10 ml of 6 *N* HNO_3, pouring the acid repeatedly through the filter. To the solution add from a dropper 1–3 drops of 0.3 *N* $Co(NO_3)_2$ solution. Evaporate the mixture to dryness and add 1–3 ml of 3 *N* Na_2CO_3 solution. Evaporate again to dryness in a porcelain dish, and ignite the residue at a temperature below redness, keeping the dish in motion, until the purple color due to cobalt disappears. Cool and moisten the residue with water. A green residue shows the presence of zinc. If the mass becomes black, owing to strong heating, add a few drops of HNO_3, evaporate to dryness, add Na_2CO_3 solution as before, evaporate, and again ignite.

12. Acidify the filtrate from § 2 with HCl, adding 5 ml of the 6 *N* acid at first and then 2 ml at a time, cooling after each addition to avoid reducing the chromate to chromic salt. Add 5 ml of 3 *N* NH_4Cl solution and 6 *N* NH_4OH till the mixture after shaking and blowing away the vapors smells of NH_3. Finally add 5 ml more of NH_4OH, heat to boiling, filter off the $Al(OH)_3$ precipitate and wash it with hot water. Examine the filtrate for chromium and zinc by § 14, and prove that the precipitate is $Al(OH)_3$ by § 13.

13. To apply the aluminon test, dissolve the precipitate in 5 ml of *N* HCl and add 5 ml of 3 *N* ammonium acetate solution and 5 ml of 0.1 per cent aqueous aluminon solution (p. 191). Mix well and make alkaline with a mixture of NH_4OH and $(NH_4)_2CO_3$. A bright red insoluble lake, persisting in the ammoniacal solution, shows the presence of aluminum. To confirm the aluminum by the Thénard blue reaction, proceed according to page 194.

14. To the filtrate obtained in § 12 add 15 ml of 3-normal sodium carbonate solution and evaporate in a porcelain casserole until no more vapors of ammonia are evolved. Then, if zinc is present, a white precipitate of basic zinc carbonate will appear. Filter and wash with hot water. Examine the precipitate by § 15 and the filtrate by § 16.

15. Dissolve the precipitate obtained in § 14 by means of 10 ml of hot 3-normal hydrochloric acid. Make the solution ammoniacal, and add 3 ml of 6-normal ammonium hydroxide in excess. If much zinc is present it will precipitate at the neutral point but redissolve in the ex-

cess of ammonia. If any precipitate remains of $Al(OH)_3$, $Cr(OH)_3$, or H_2SiO_3, filter it off and discard it. Make the solution slightly acid with acetic acid and saturate with hydrogen sulfide. A white precipitate of zinc sulfide shows the presence of *zinc*.

16. To the filtrate from § 14, add acetic acid to acid reaction and 20 ml of water, heat to boiling and add a little lead acetate solution. A yellow precipitate of lead chromate is formed if *chromium* is present. A white precipitate of lead chloride which usually forms on cooling has no significance. Chromate anions are distinctly yellow in color, and it is unnecessary to test with lead acetate unless the solution is yellow.

Quiz Questions. Precipitation of Group III

1. In parallel columns write (*a*) formulas of substances of Group III pptd. by NH_4OH, (*b*) by $(NH_4)_2S$, (*c*) the colors of the ppts., (*d*) product of action of HCl and HNO_3 on (*a*) and (*b*), and (*e*) product of action of NaOH and Na_2O_2 on each of (*d*).

2. (*a*) If the elements of the silver group are not pptd. by first adding NH_4Cl, where would they appear? Explain carefully.

(*b*) If Pb were not completely pptd. by H_2SO_4 where would it appear? Show by equations how it gets there.

3. Why test for phosphate in the analysis for cations? Give an equation for the test. Write an equation to show the effect of $KClO_3$ in dissolving the sulfide ppt. Why expel H_2S before adding NH_4OH? Why is it sometimes better to pass H_2S into an ammoniacal soln. than to add $(NH_4)_2S$?

4. Complete and balance:

(*a*) $Fe_2S_3 + H^+$ (*b*) $NiCl_2 +$ excess NH_4OH

(*c*) $MnCl_2 + Na_2O_2 + H_2O$ (*d*) $Al_2S_3 + H_2O$ (*e*) $CrCl_3 + Na_2O_2 + H_2O$

5. (*a*) If in an actual anal. the mixt. contg. ammonia and ammonium sulfide were allowed to absorb CO_2 from the air before filtering, what would be the effect?

(*b*) What constituents are present in a soln. of ammonium sulfide?

(*c*) Why is H_2S boiled off before adding ammonium sulfide?

6. (*a*) Why doesn't Al_2S_3 ppt. when $(NH_4)_2S$ is added? (*b*) $Mg(OH)_2$ is insol. in water. Why doesn't it ppt. when "magnesium nitrate reagent" is prepared by dissolving a mixt. of $Mg(NO_3)_2$, $(NH_4)NO_3$, and NH_4OH in water?

7. If 200 ml of Na_2CrO_4 soln. contg. 0.520 g of Cr is made 0.3 *N* with HCl, satd. with H_2S and the pptd. S is removed, how many ml of 6 *N* NH_4OH will be required to neutralize the soln. and how much more for the complete pptn. of $Cr(OH)_3$?

8. Find the p_H of a soln. contg. 3 milliequivalents of HCl and 5 g of $NaC_2H_3O_2 \cdot 3\,H_2O$ in 600 ml of soln. Assume the salt completely ionized and the ionization const. of acetic acid 1.8×10^{-5}.

9. Find the p_H of a soln. contg. 3 ml of 6 *N* NH_4OH and 5 g of NH_4Cl in a vol. of 400 ml. Assume the salt to be completely ionized and the ionization const. of the base to be 1.8×10^{-5}.

10. The *Sp* of $Mg(OH)_2$ is 3.4×10^{-11} and of $Fe(OH)_3$ is 1.1×10^{-36}. Find the p_H value of the soln. below which 1 mg of Mg^{++} will not ppt., and the p_H value below which 1 mg of Fe^{+++} will not ppt. as hydroxides. Assume $[H^+] \times [OH^-] = 10^{-14}$.

11. Find the p_H of (*a*) 0.0028 *N* NaOH, (*b*) 0.028 *N* $HC_2H_3O_2$ and (*c*) 0.028 *N* NH_4OH, assuming the strong base to be completely ionized and the ionization constants of both the weak acid and the weak base to be about 1.8×10^{-5}. Assume $[H^+] \times [OH^-] = 10^{-14}$.

Quiz Questions. Aluminum Group

1. Give a tabular outline of the analysis of the Al group.

2. Complete and balance equations showing:

(*a*) Two stages in the action of HCl on $NaAlO_2$.

(*b*) Two stages in the action of HCl on $NaZnO_2$.

(*c*) $Cr^{+++} + NaBiO_3 + H^+ \rightarrow$ (*e*) $Zn^{++} +$ excess $NH_4OH \rightarrow$

(*d*) $Cr_2O_7^{--} + H_2S + H^+ \rightarrow$ (*f*) $Cr^{+++} + OH^- + Na_2O_2 \rightarrow$

3. Complete the equations:

(*a*) $NaAlO_2 + HNO_3$ (1 equivalent)
(*b*) $NaAlO_2 + HNO_3$ (in excess)
(*c*) $Co(NO_2)^2 + Al(NO_3)_3$ (dried and heated)
(*d*) $BaCrO_4 + HCl + H_2SO_3$
(*e*) $Na_2ZnO_2 + HNO_3$ (2 equivalents)
(*f*) $Na_2ZnO_2 + HNO_3$ (in excess)

4. Would you expect any hydroxide which does not form a complex ammine to be sol. in an excess of NH_3 soln. and not in NaOH soln.? Can a hydroxide be readily sol. in NaOH soln. and practically insol. in an excess of NH_4OH?

5. Given 500 mg of Cr as chromate in the presence of excess HCl. How many ml of sulfurous acid, density 1.04, contg. 10 per cent SO_2 by wt., will be required to reduce the CrO_4^{--} to Cr^{+++}?

6. A neutral soln. contained 150 mg of Ag, 200 mg of Cd, and 250 mg of Mn as MnO_4^-; 5 ml of 6 *N* HNO_3 and 5 ml of *N* NH_4Cl soln. were added and the ppt. removed by filtration, then H_2S was introduced.

(*a*) Write balanced equations for all the changes taking place as well as for those resulting on adding NH_4OH to the filtrate after boiling out the H_2S.

(*b*) Calc. how many ml of 6 *N* NH_4OH must be added to just neutralize the filtrate from the H_2S ppt.

7. (*a*) Can NH_4AlO_2 exist in the presence of water? What happens when it is boiled with water? Equation.

(*b*) If in an actual analysis no ppt. is obtained on adding NH_4OH before adding $(NH_4)_2S$ to ppt. the Fe and Al groups, what elements are supposedly absent?

8. (*a*) Write equilibrium equations for the relation between CrO_4^{--} and $Cr_2O_7^{--}$.

(*b*) Name four reducing agents which act upon CrO_4^{--} in acid soln. Illustrate by balanced equations.

9. (*a*) In the final pptn. of Al by means of excess NH_4OH, why isn't Cr pptd.? Why isn't Zn? What is the harm of adding a large excess of NH_4OH?

(*b*) What are the colors of separate solns. of $K_2Cr_2O_7$, $Cr(AcO)_3$, Na_2CrO_4?

(*c*) What is meant by adsorption? How is it illustrated in the confirmatory test for Al?

10. Given 520 mg of Cr as chromate, how many ml of 0.125 *N* $SnCl_2$ soln. will react with it in the presence of HCl?

Quiz Questions. Iron Group

1. In the qual. anal. of a soln. contg. $KMnO_4$, $FeCl_3$, $Zn(NO_3)_2$ and $Ca_3(PO_4)_2$ dissolved in HNO_3, write balanced equations to show what happens at each of the following stages of the anal.:

(*a*) The soln. after treatment with NH_4Cl is satd. with H_2S.
(*b*) After removal of the excess H_2S, the filtrate from (*a*) is treated with NH_4OH.
(*c*) Without filtering, the soln. is treated with $(NH_4)_2S$.

2. Complete and balance the following equations:

$Ca^{++} + PO_4^{---} + NH_4OH \rightarrow$
$Ca^{++} + Fe^{+++} + PO_4^{---} + NH_4OH \rightarrow$
$Fe^{+++} + C_2H_3O_2^- + H_2O \rightarrow$
$Fe^{++} + NaOH + Na_2O_2 \rightarrow$
$Mn^{++} + NaOH + Na_2O_2 \rightarrow$
$Mn^{++} + NaBiO_3 + H^+ \rightarrow$

3. Outline the tin and $BaCO_3$ methods as used instead of the basic acetate procedure for removing H_3PO_4.

4. Describe the behavior of Fe^{++} and Fe^{+++} toward $[Fe(CN)_6]^{----}$, $[Fe(CN)_6]^{---}$ and CNS.

5. If no Fe is present and a soln. contains 0.248 g of P as phosphate, how many ml of *N* $Fe(NO_3)_3$ soln. should be added to prevent pptn. of alk. earth phosphate on neutralization?

6. If the ionization const. of HAcO is 1.8×10^{-5}, calc. the concn. of H^+ in moles per l. (*a*) in 0.1 *N* HAcO soln. and (*b*) in 250 ml of soln. contg. 6.0 g of HAcO (mol. wt. 60) and 16.4 g of $NaAcO \cdot 3\,H_2O$ (mol. wt. 136).

7. Complete and balance the following equations:

(*a*) $MnO_2 . H_2O + HNO_3 + H_2O_2$
(*b*) $Co(OH)_3 + HNO_3 + H_2O_2$
(*c*) $MnO_4^- + H_2O_2 + HNO_3$
(*d*) $BiO_3 + HNO_3 + Mn^{++}$
(*e*) $Mn^{++} + HClO_3$
(*f*) Fe^{+++} + excess NH_4OH

8. State what conditions are most likely to cause a part of any Zn present to appear in the Fe group. What is the probable explanation of this?

9. $Mg(OH)_2$ is not very sol. in water. Why then is it not pptd. when NH_4OH and $(NH_4)_2S$ are added to ppt. the Fe and Al groups? When is magnesium likely to ppt with Group III?

10. A neutral soln. contains 50 mg of Ag^+, 200 mg of Cd^{++}, and 250 mg of Mn as MnO_4^-; 5 ml of 6 *N* HNO_3 and 5 ml of 1 *N* NH_4Cl are added and the ppt. filtered off. Then the soln. is diluted to

100 ml and satd. with H_2S. How many ml of 6 *N* NH_4OH must now be added to bring the soln. to just the neutral point? Write equations for the reaction of each constituent. In the calculation show clearly the effect produced by each constituent, and designate each of the intermediate results.

Quiz Questions. Nickel, Cobalt, etc.

1. How is the H_2S for the laboratory prepared? How could H_2S be prepared from pyrite? Assuming the laboratory gas to be 40 per cent H_2 and 60 per cent H_2S, what vol. measured at 20° and 750 mm pressure would be required to ppt. 0.5868 g of Ni from ammoniacal soln.?

2. Complete and balance equations representing the reactions indicated:

(*a*) Ni^{++} and the dimethylglyoxime test.
(*b*) Co^{++} and the cobaltinitrite test.
(*c*) Borax bead and CoO.
(*d*) $CoCl_2$, KCN and Br in presence of KOH.
(*e*) Same reaction with $NiCl_2$.

3. If a student is given a mixt. of solid $MgCrO_4$, $Mn_3(PO_4)_2$ and $CaCO_3$ explain what will happen:

(*a*) When the powder is treated with water.
(*b*) When acid is added.
(*c*) When H_2S is added.
(*d*) When NH_4OH and $(NH_4)_2S$ are added.
(*e*) When the ppt. produced in (*d*) is analyzed in accordance with the scheme for the Al and Fe groups.

4. Make a tabular synopsis of the Fe group (including the sepn. of the Ni and Co) in the absence of phosphate; state the colors, formulas, and solys. of all substances of importance in the identifications.

5. What happens to $Zn(NO_3)_2$ and to $Co(NO_3)_2$ when they are ignited separately? What happens in the confirmatory test for Zn?

6. Write equations showing how Co^{++} can be converted into $Co(OH)_2$, $K_4Co(NO_2)_6$, and $K_4Co(CN)_6$. State how Ni^{++} behaves under similar treatment.

7. If a ppt. contg. FeS, MnS, NiS, and CoS was analyzed by the procedure given for Group II, where would the Fe, Mn, Ni, and Co give indications of their presence?

8. If Cu, Bi, Zn, and Cd were not pptd. in the proper place, how would these elements interfere with the analysis of Group III?

GROUP IV. ALKALINE EARTHS AND MAGNESIUM

CALCIUM, STRONTIUM, BARIUM, MAGNESIUM

GENERAL CHARACTERISTIC REACTIONS

The metals of the alkaline earth group are bivalent and heavier than water, which they decompose slowly at ordinary temperatures, with evolution of hydrogen and formation of difficultly soluble hydroxides of strongly alkaline reaction (cf. p. 44). The salts are mostly colorless and very slightly soluble in water. The halogen compounds, nitrates, nitrites, and acetates are soluble in water. The carbonates are insoluble in water and are decomposed on ignition into carbon dioxide, and white, infusible, strongly luminous metallic oxide:

$$CaCO_3 \rightleftarrows CaO + CO_2\uparrow$$

Strontium carbonate is less readily decomposed than calcium carbonate, and barium carbonate loses its carbon dioxide only when heated to a white heat; its oxide is not very luminous.

The sulfates and oxalates are very difficultly soluble. The sulfate of barium is the most insoluble sulfate, and calcium sulfate the most soluble; of the oxalates, the calcium salt is the most insoluble (cf. p. 277). The solubility of the strontium salt is always midway between that of the corresponding calcium and barium salt, for the atomic weight of strontium, of which the solubility is a function, lies midway between the atomic weights of barium and calcium. The halogen salts are volatile and impart a characteristic color to the flame.

The metals of this group form oxides of the general type RO, and peroxides corresponding to the formula RO_2. The latter, on treatment with acids, give hydrogen peroxide and salts corresponding to the oxide RO:

$$RO_2 + 2\,HCl \rightarrow H_2O_2 + RCl_2$$

Magnesium is more closely related to this group than to the alkali metals. It can be precipitated with this group if the group precipitant, ammonium carbonate, is added to the concentrated solution together with an equal volume of alcohol.

CALCIUM, Ca. At. Wt. 40.08, At. No. 20

Density 1.55. M. P. 810°. B. P. 1712° ± 5°

Occurrence. — Calcium is widely distributed in nature. It is found in enormous deposits in all stratified formations as carbonate (lime-stone, marble, chalk), often rich in petrifaction. The carbonate, $CaCO_3$, is dimorphous, crystallizing in rhom-

bohedrons as calcite and in the orthorhombic system as aragonite. Calcium also occurs in large masses as sulfate, partly as monoclinic crystallizing gypsum, $CaSO_4 \cdot 2\,H_2O$, and partly as anhydrite, $CaSO_4$, which crystallizes in the orthorhombic system. Calcium also occurs as fluorite, CaF_2, which crystallizes in the isometric system, with perfect octahedral cleavage; as apatite, $3\,Ca_3(PO_4)_2 \cdot Ca\begin{matrix}Cl\\F\end{matrix}$, which belongs to the hexagonal system; and, finally, in innumerable silicates, such as the monoclinic wollastonite, $CaSiO_3$, and the triclinic anorthite, $CaAl_2Si_2O_8$. The calcium minerals are the principal representatives of several important isomorphous groups:

Calcite Group,	*Rhombohedral.*	*Aragonite Group,*	*Orthorhombic.*
Calcite,	$CaCO_3$	Aragonite,	$CaCO_3$
Magnesite,	$MgCO_3$	Strontianite,	$SrCO_3$
Dolomite,	$\begin{matrix}Ca\\Mg\end{matrix}\Big\} CO_3$	Witherite,	$BaCO_3$
		Cerussite,	$PbCO_3$
Siderite,	$FeCO_3$		
Smithsonite,	$ZnCO_3$		
Rhodochrosite,	$MnCO_3$		

Anhydrite Group,	*Orthorhombic.*	*Apatite Group,*	*Hexagonal.*
Anhydrite,	$CaSO_4$	Apatite,	$3\,Ca_3(PO_4)_2 + Ca(Cl, F)_2$
Celestite,	$SrSO_4$	Pyromorphite,	$3\,Pb_3(PO_4)_2 + PbCl_2$
Barite,	$BaSO_4$	Mimetite,	$3\,Pb_3(AsO_4)_2 + PbCl_2$
Anglesite,	$PbSO_4$	Vanadinite,	$3\,Pb_3(VO_4)_2 + PbCl_2$

Properties. — Metallic calcium, first obtained by Davy in 1808, is silver-white when pure. It oxidizes in the air, forming calcium hydroxide, $Ca(OH)_2$, and calcium carbonate, $CaCO_3$. It decomposes water with evolution of hydrogen and formation of the hydroxide. It dissolves in mercury to form an amalgam. Small quantities of calcium are sometimes alloyed with lead as a hardener. Metallic calcium is obtained by the electrolysis of fused calcium chloride.

The name *calcium* is derived from the Latin *calx* = lime.

Calcium oxide, CaO, or *quicklime*, reacts readily with water liberating much heat (slaking of lime). The hydroxide (slaked lime) is much less soluble in water than are barium and strontium hydroxides and is formed upon the addition of alkali hydroxide to a concentrated solution of a calcium salt. Air-slaked lime contains calcium carbonate.

Calcium peroxide, $CaO_2 \cdot 8\,H_2O$, is made by adding H_2O_2 or Na_2O_2 to the hydroxide. The chloride and the nitrate of calcium are soluble in absolute alcohol or in a mixture of equal parts of alcohol and ether. Of the corresponding barium and strontium salts only the chloride of strontium is soluble in alcohol.

Calcium nitrate is much more soluble than barium nitrate in strong nitric acid, and the chloride is much more soluble than barium chloride in hydrochloric acid.

Reactions in the Wet Way

1. **Absolute Alcohol**, or a mixture of equal parts of absolute alcohol and ether, dissolves both the nitrate and chloride of calcium.

All deliquescent salts, with the exception of potassium carbonate, dissolve in absolute alcohol. All other salts are, in general, insoluble, or

very difficultly soluble, in absolute alcohol. An exception to this rule is found in mercuric chloride, which is not deliquescent, and is much more readily soluble in alcohol than in water.

2. **Ammonia,** provided that it is free from carbonate, produces no precipitate with calcium salts; on standing in the air, however, carbonic acid is absorbed and a turbidity of calcium carbonate results.

3. **Ammonium Carbonate,** or any other soluble, normal carbonate, precipitates white calcium carbonate; the precipitate is voluminous and flocculent when it first forms, but soon becomes crystalline, particularly when in contact with boiling water:

$$Ca^{++} + CO_3^{--} \rightarrow CaCO_3 \qquad (I)$$

The precipitate is noticeably soluble in an aqueous solution of the ammonium salt of any strong acid:

$$CaCO_3 + 2\,NH_4^+ \rightarrow Ca^{++} + 2\,NH_3 \uparrow + H_2O + CO_2 \uparrow \qquad (II)$$

When ammonium carbonate is the precipitant, equation (II) is essentially the opposite to equation (I) and the mass-action law shows how the reaction can be made to go in either direction. An excess of ammonium carbonate will favor the progress of equation (I), and boiling with a large quantity of an ammonium salt such as ammonium chloride will cause equation (II) to go to completion.

Ammonium carbonate is an unstable substance (cf. p. 294). Commercial ammonium carbonate, often called ammonium sesquicarbonate, is a mixture of approximately equivalent quantities of ammonium bicarbonate, NH_4HCO_3, and ammonium carbamate, $NH_4CO_2NH_2$; the latter salt corresponds to normal ammonium carbonate less one molecule of water. Calcium carbamate is quite soluble in water but by contact with water at 60° it becomes changed to insoluble calcium carbonate. The ammonium carbonate reagent is prepared with 6 *N* ammonia instead of water; this prevents the hydrolysis of the salt and changes the bicarbonate to ammonium carbonate.

Calcium bicarbonate is soluble in water, so that any acid which is dissociated to a greater extent than HCO_3^- will exert a solvent effect upon calcium carbonate:

$$CaCO_3 + H^+ \rightleftarrows Ca^{++} + HCO_3^-$$

Thus acetic acid dissolves calcium carbonate readily. Boiling the solution favors the progress of the reaction, since the HCO_3^- is also in equilibrium with H^+ and H_2CO_3 and the latter with H_2O and CO_2:

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow H_2O + CO_2 \uparrow$$

and the carbon dioxide can be expelled completely at 100° (cf. p. 30).

The precipitation of calcium carbonate from boiling dilute solutions containing ammonium salts is always more or less incomplete, for the reasons that have just been given, but from cold concentrated solutions containing considerable alcohol the precipitation is practically complete.

4. **Ammonium Ferrocyanide** gives with calcium salts a white crystalline precipitate of $Ca(NH_4)_2[Fe(CN)_6]$. If 1 drop of the solution to be tested is stirred with a few drops of a concentrated $(NH_4)_4Fe(CN)_6$ solution and 1 drop of alcohol, a crystalline precipitate will form if 0.025 mg of calcium is present or a turbidity with less than 0.05 γ.

5. **Ammonium Oxalate** produces in neutral or alkaline solutions a precipitate of calcium oxalate, which when formed from cold solutions is composed of extremely fine crystals, hard to filter, while from hot solutions larger crystals are formed:

$$C_2O_4^{--} + Ca^{++} \rightleftarrows \mathbf{CaC_2O_4}$$

Calcium oxalate is practically insoluble in water and acetic acid, but dissolves readily in mineral acids:

$$\mathbf{CaC_2O_4} + 2\,H^+ \rightleftarrows Ca^{++} + H_2C_2O_4$$

Calcium oxalate, unlike calcium carbonate, does not dissolve in acetic acid for the following reasons: (1) The solubility product of calcium oxalate is about 2×10^{-9} while that of calcium carbonate is about 1.7×10^{-8} (p. 22), which shows that the oxalate is somewhat less soluble in water than the carbonate. (2) The ionization constant of HCO_3^- is $0.0_{10}5$, while that of $HC_2O_4^-$ is 0.0_46 and that of acetic acid is 0.0_417; this is sufficient to explain why acetic acid has little solvent effect upon calcium oxalate. To dissolve calcium oxalate readily it is necessary to use an acid strong enough to repress the ionization of the first hydrogen of oxalic acid, for which the ionization constant is 0.065. (3) The progress of the reaction cannot be aided, as in the case of the carbonate, by the loss of a volatile constituent.

Ammonia reprecipitates from such a solution calcium oxalate; the excess of hydrogen ions, as well as the oxalic acid which was formed are neutralized.

Calcium oxalate on being boiled with sodium carbonate solution is easily changed to carbonate:

$$\mathbf{CaC_2O_4} + CO_3^{--} \rightleftarrows \mathbf{CaCO_3} + C_2O_4^{--}$$

This reaction takes place in the direction left to right when a large excess of CO_3^{--} ions is present in spite of the fact that calcium oxalate is somewhat less soluble than calcium carbonate. This is in accordance with the mass-action law (p. 2). An excess of $C_2O_4^{--}$ ions will make the reaction take place in the direction right to left.

6. **Barium Fluoride** precipitates calcium fluoride, CaF_2. The presence of 0.8 mg in 10 ml of solution can be shown by this reagent.

7. **Calcium Sulfate** solution produces no precipitation with calcium salts. (Note difference from strontium and barium.)

8. **Chromates of the Alkalies** do not precipitate calcium salts from dilute solution. (Note difference from barium and strontium.) In a *concentrated* solution of calcium salt to which potassium chromate has been added, a precipitate of calcium chromate, $CaCrO_4 \cdot 2\,H_2O$, forms slowly after some time, or immediately upon adding two or three volumes of alcohol. Adding ammonium hydroxide favors the precipitation, but acetic acid prevents it.

9. **The osazone of dihydroxytartaric acid,**

$$\begin{array}{l} C_6H_5NH - N = C - COOH \\ \qquad\qquad\qquad\quad | \\ C_6H_5NH - N = C - COOH, \end{array}$$

yields in aqueous solutions of alkaline earth salts a yellow flocculent precipitate in which the hydrogen atoms of the two carboxyl groups are replaced by alkaline earth. As reagent the solid sodium salt is used; it will show the presence of as little as 0.01 γ of calcium and will usually give the test in a drop of the mixture of 1 part of tap water with 30 parts of distilled water. To carry out the test, place 1 drop of the solution to be tested on a blackened spot plate or watch glass and add a tiny fragment of the reagent.

10. **Sodium Phosphate** (Na_2HPO_4) produces in neutral solutions a white, flocculent precipitate of secondary calcium phosphate:

$$Ca^{++} + HPO_4^{--} \rightarrow CaHPO_4$$

If ammonia is added to the solution at the same time, tertiary calcium phosphate will be precipitated:

$$HPO_4^{--} + OH^- \rightarrow H_2O + PO_4^{---}$$
$$3\,Ca^{++} + 2\,PO_4^{---} \rightarrow Ca_3(PO_4)_2$$

Both of these phosphates of calcium are dissolved by hydrogen ions. A glance at the table on page 16 shows that even acetic acid will repress the ionization of $H_2PO_4^-$ to an extent such that it will exert a slight solvent action upon $CaHPO_4$ and upon $Ca_3(PO_4)_2$. Acetic acid in the presence of a soluble acetate, however, will not dissolve $Ca_3(PO_4)_2$ appreciably. From a solution obtained by dissolving calcium phosphate in acid, ammonia always precipitates the tertiary salt.

11. **Sulfuric Acid** produces a precipitate only in concentrated solutions:

$$CaCl_2 + H_2SO_4 \rightleftarrows 2\,HCl + CaSO_4$$

The precipitation is complete, however, if the solution contains about 75 per cent of ethyl alcohol, C_2H_5OH.

One hundred ml of water dissolves 0.214 g $CaSO_4 \cdot 2\,H_2O$ at 40°, but much less than 1 mg will dissolve in the same quantity of alcohol. In the presence of a slight excess of sulfate ions, calcium sulfate is less soluble, but the behavior of calcium sulfate toward hydrogen ions is similar to that of calcium carbonate. Calcium acid sulfate is much more soluble than normal calcium sulfate, and any acid which is capable of repressing the ionization of HSO_4^- will exert a solvent effect upon $CaSO_4$. Sulfuric acid itself, or any other strong acid, can exert this solvent effect.

Calcium sulfate is also soluble in concentrated ammonium sulfate, owing to the formation of a complex anion:

$$CaSO_4 + (NH_4)_2SO_4 \rightarrow (NH_4)_2[Ca(SO_4)_2]$$

12. **Water** decomposes the carbide, phosphide, and nitride of calcium at ordinary temperatures, as follows:

(*a*) The carbide:

$$CaC_2 + 2\,HOH \rightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}\uparrow$$

Acetylene is evolved by the reaction, a gas with a peculiar odor.* If this gas is conducted into an ammoniacal copper solution, it rapidly produces a red precipitate of copper acetylide. The latter compound is harmless while it is moist; but in the dry state it can be readily exploded by a blow, by rubbing, or by simply warming.

(*b*) The phosphide:

$$Ca_3P_2 + 6\,HOH \rightarrow 2\,Ca(OH)_2 + 2\,PH_3\uparrow$$

Phosphine gas which is evolved with a garlic-like odor is spontaneously combustible, because it always contains a small amount of the liquid hydrogen phosphide (P_2H_4).

(*c*) The nitride:

$$Ca_3N_2 + 6\,HOH \rightarrow 2\,Ca(OH)_2 + 2\,NH_3\uparrow$$

Reactions in the Dry Way

Calcium compounds, on being heated with sodium carbonate before the blowpipe, are changed to the white infusible oxide, which glows brightly when hot.

The volatile calcium compounds color the non-luminous gas flame brick-red.

Flame Spectrum. — Orange-yellow double line (620.3 mμ, 618.2 mμ) and a yellowish green one (554.4 mμ, 551.8 mμ); both these lines belong to calcium oxide. If calcium chloride wet with hydrochloric acid is placed in the flame, a number of other lines are seen; in the orange-yellow 646.6 mμ, 606.9 mμ, 604.5 mμ, and 593.4 mμ, in the yellow 581.7 mμ and 572.0 mμ, in the violet, usually very difficult to see, 422.7 mμ.

STRONTIUM, Sr. At. Wt. 87.63, At. No. 38

Density 2.6. M. P. 752° ± 2°. B. P. 1639° ± 5°

Occurrence. — Strontium occurs quite commonly with calcium, but usually in much smaller amounts. There are only a few true strontium minerals. The most important of these are: Strontianite, $SrCO_3$, orthorhombic, isomorphous with aragonite; and celestite, $SrSO_4$, orthorhombic, isomorphous with barite.

Properties. — Metallic strontium is described generally as a silver-white metal, but some authorities ascribe to it the color of brass; the yellow tint is probably due

* Pure acetylene is odorless. Almost all calcium carbide contains a little calcium phosphide, which evolves phosphine on treatment with water.

to impurities. It is similar to calcium in its chemical behavior. It is prepared by the electrolysis of an aqueous solution of its chloride with a mercury cathode. The amalgam obtained is heated in hydrogen to drive off the mercury. It can also be obtained by heating the oxide with aluminum in a vacuum furnace at 1000°. The hydroxide is more soluble in water than calcium hydroxide is, and it requires stronger heating to convert it into the oxide.

The name *strontium* is from *Strontian*, a town in Scotland. The metal itself has been available commercially since 1929, but there is very little demand for it. The hydroxide is used in the beet sugar industry and the nitrate for fireworks and red fire signals. The United States imports about 1,500 tons of strontium chemicals and ores annually.

The white strontium oxide, SrO, is formed by heating the hydroxide, carbonate, nitrate, or salt of any organic acid. A higher temperature is required than in the case of calcium. About 0.7 g of SrO dissolves in 100 ml of water. The peroxide, $SrO_2 \cdot 8\ H_2O$, is obtained by treating the hydroxide with hydrogen peroxide. It is only slightly soluble in water or ammonia solution but dissolves readily in acid or in a solution containing ammonium chloride.

Reactions in the Wet Way

1. **Absolute Alcohol.** The nitrate is not deliquescent, and does not dissolve in absolute alcohol. Strontium chloride is slightly deliquescent; the anhydrous salt dissolves scarcely at all in absolute alcohol; but, on the other hand, 1 g of $SrCl_2 \cdot 6\ H_2O$ dissolves in 116.4 g of cold alcohol and 262 g of boiling absolute alcohol.

2. **Ammonia:** same as with calcium.

3. **Ammonium Carbonate:** same as with calcium.

4. **Ammonium Oxalate:** same as with calcium; but the strontium oxalate is somewhat soluble in acetic acid.

5. **Calcium Sulfate** solution produces in neutral or weakly acid solutions, *after some time*, a precipitate of strontium sulfate:

$$Sr^{++} + CaSO_4 \rightarrow SrSO_4 + Ca^{++}$$

6. **Chromates of the Alkalies** produce in dilute solutions no precipitate (difference from barium); but from concentrated solutions strontium chromate is precipitated. It is much less soluble in alcohol; 100 ml of alcohol, 53 per cent by volume, will dissolve 0.002 g $SrCrO_4$ and 0.088 g of $CaCrO_4$ at room temperature; 100 ml of 29 per cent alcohol will dissolve 0.132 g $SrCrO_4$ and 1.22 g $CaCrO_4$. The precipitate is quite soluble in acetic acid.

7. **Dilute Sulfuric Acid** produces a white precipitate of strontium sulfate:

$$SrCl_2 + H_2SO_4 \rightarrow 2\ HCl + SrSO_4$$

Strontium sulfate is much less soluble in water than calcium sulfate (6,900 parts of water at ordinary temperatures dissolve 1 part $SrSO_4$),

but much more soluble than barium sulfate. It is somewhat soluble in boiling hydrochloric acid, and insoluble in ammonium sulfate. By boiling with a solution of ammonium or alkali carbonate solution, the strontium sulfate is changed to carbonate:

$$SrSO_4 + CO_3^{--} \rightleftarrows SrCO_3 + SO_4^{--}$$

8. **Sodium Rhodizonate,** $Na_2C_6O_6$, gives brownish red precipitates with Ba and Sr in neutral solutions. As little as 3.9 γ of Sr can be detected by the following spot test in which the Ba is converted into insoluble $BaCrO_4$. Impregnate some filter paper with K_2CrO_4 by moistening it with a saturated solution and drying. Touch the paper with a drop of the solution to be tested, and after one minute touch the same spot with a drop of 5 per cent sodium rhodizonate solution (Feigl).

9. **Sodium Sulfite** precipitates strontium sulfite from neutral or acetic acid solutions; the precipitate is soluble in hydrochloric acid.

Reactions in the Dry Way

Heated on charcoal before the blowpipe the strontium compounds behave similarly to the calcium compounds.

The volatile strontium salts color the non-luminous gas flame carmine red.

Flame Spectrum. — A number of lines in the red and orange-yellow and one in the blue. No bands in the green. Red 686.3 mμ, 674.7 mμ, 662.8 mμ, 649.9 mμ; orange-yellow 646.5 mμ, 635.1 mμ, **606.0** mμ; blue **460.7** mμ.

BARIUM, Ba. At. Wt. 137.36, At. No. 56

Density 3.5. M. P. 850°. B. P. 1140°

Occurrence. — Like strontium, barium is almost always found associated with calcium, but only in small amounts. The most important barium minerals are: Witherite, $BaCO_3$, orthorhombic, ismorphous with aragonite; barite, or heavy spar, $BaSO_4$, orthorhombic, isomorphous with anhydrite; and the hydrous barium aluminum silicate, harmotome, $BaAl_2H_2Si_5O_{15} \cdot 4\,H_2O$. Harmotome crystallizes in the monoclinic system, and belongs to the class of zeolites. The name barium comes from the Greek word *barys* = heavy. The principal mineral is called *heavy spar* = $BaSO_4$.

Properties. — Metallic barium is usually described as of silver-white color but according to some observers it is gold-yellow. Concentrated solutions of barium salts give precipitates of barium chloride upon the addition of strong hydrochloric acid and of barium nitrate upon the addition of strong nitric acid. Insoluble barium salts, therefore, dissolve more readily in dilute hydrochloric or nitric acid than in stronger acid. Soluble barium salts are poisonous. About 350,000 tons of barite are mined annually in the United States. Barium sulfate in a very fine state of subdivision is the *blanc fixe* used in paints, so called because the paint does not darken, as does white lead, when exposed to air containing hydrogen sulfide. Barium sulfate is an ingredient of lithopone paint. A small quantity of metallic barium is used

industrially, *e.g.*, as a "getter" in radio tubes and alloyed with nickel for ignition systems of gasoline engines. The metal is worth about $35 per pound. It can be prepared by the electrolysis of the fused chloride or by the electrolysis of an aqueous solution with a mercury cathode; in the latter case an amalgam is obtained from which the mercury is removed by heating in hydrogen. Barium peroxide, BaO_2, is formed by heating BaO to 500–600° in oxygen. Further heating decomposes the BaO_2 into BaO and O_2. Hydrogen peroxide is obtained by dissolving the barium peroxide in acid.

The hydroxide, $Ba(OH)_2$, is much more soluble in water than are the hydroxides of the other alkaline earths and it melts undecomposed at a red heat. About 3 g dissolves in 100 ml of water at room temperature and about 100 g dissolves at the temperature of boiling. In the air, the solution soon becomes turbid by absorption of CO_2 and precipitation of $BaCO_3$. The oxide can be obtained by ignition of the hydroxide, carbonate, nitrate, or salt of an organic acid. The temperature required is, however, much higher than with strontium and calcium salts. Thus, by heating to about 900°, it is easy to accomplish the complete conversion of a calcium oxalate precipitate to calcium oxide in quantitative analysis, but similar heating of a barium oxalate precipitate in a platinum crucible gives barium carbonate and very little, if any, barium oxide.

Reactions in the Wet Way

1. **Absolute Alcohol** dissolves neither the nitrate nor the chloride; neither of these salts is deliquescent. One hundred ml of 66 per cent alcohol (by volume) dissolves 3.3 g of $BaCl_2 \cdot 2\,H_2O$.

2. **Ammonia** and **Ammonium Carbonate:** same as with calcium and strontium.

3. **Ammonium Oxalate:** same as with calcium and strontium, except that the barium oxalate formed is more soluble in water (1 g dissolves in 2.6 l of cold water) and is readily dissolved by hot dilute acetic acid.

4. **Chromates of the Alkalies** produce in neutral solutions of barium salts a yellow precipitate of barium chromate (difference from calcium and strontium):

$$Ba^{++} + CrO_4^{--} \rightleftarrows \mathbf{BaCrO_4}$$

The table on page 11 shows that $HCrO_4^-$ is ionized only to between 0.1 and 0.2 per cent in 0.1 *N* solution. In the presence of a stronger acid, its ionization becomes much less, and the equilibria

$$H^+ + CrO_4^{--} \rightleftarrows HCrO_4^- \text{ and } 2\,HCrO_4^- \rightarrow H_2O + Cr_2O_7^{--}$$

progress farther in the direction left to right than in pure water. The final equilibrium, however, also depends upon the concentration of CrO_4^{--} in the solution. In the saturated aqueous solution of strontium chromate, enough CrO_4^{--} ions are present so that the formation of the $HCrO_4^-$ takes place to a considerable extent when a little acetic acid is added, and it is easy in this way to prevent the precipitation of as much as 0.5 g of strontium ions; barium chromate, on the other hand, is so

much less soluble that it takes considerable acetic acid to have an appreciable effect upon its solubility. Thus a small quantity of barium can be separated from quite a large quantity of strontium by adding CrO_4^{--} and a suitable quantity of acetic acid.

If a more highly ionized acid is present, such as hydrochloric acid, the barium will not be precipitated as chromate, but by adding sodium acetate (cf. p. 51) the concentration of the hydrogen ions can be reduced sufficiently to precipitate even a small quantity of barium as chromate.

5. **Concentrated Hydrochloric Acid** and **Nitric Acid** will precipitate from fairly concentrated barium solutions the chloride and nitrate respectively.

6. **Dilute Sulfuric Acid,** in even the most dilute solutions, produces a precipitate of barium sulfate:

$$Ba^{++} + SO_4^{--} \rightarrow BaSO_4$$

According to the table on page 22, 1 l of pure water dissolves about 2.5 mg of barium sulfate. In a slight excess of sulfuric acid it is much less soluble by virtue of the common-ion effect (p. 30). As with strontium and barium sulfates, the presence of an excess of hydrogen ions has a solvent action due to the formation of acid sulfate. This effect is appreciable with acids such as hydrochloric or nitric acid, but the solubility of barium sulfate is so slight that it requires treatment with hot, concentrated sulfuric acid in order to get any considerable quantity of barium sulfate into solution, and dilution with water causes reprecipitation of barium sulfate:

$$BaSO_4 + H_2SO_4 \rightleftarrows Ba(HSO_4)_2$$

Barium sulfate is partially converted, as a result of the mass-action effect, into more soluble barium carbonate by boiling with a concentrated solution of sodium carbonate:

$$BaSO_4 + Na_2CO_3 \rightleftarrows BaCO_3 + Na_2SO_4$$

To make this decomposition quantitative, the barium sulfate must be boiled with the sodium carbonate solution, filtered, treated with a new portion of sodium carbonate solution, and the process repeated until the filtrate no longer gives a test for sulfate. The more concentrated the sodium carbonate solution, the more complete will be the decomposition. The highest degree of concentration will be reached by *fusion of the barium sulfate with anhydrous sodium carbonate.*

Consequently, to obtain a solution of barium ions from insoluble barium sulfate, it is best to proceed as follows: Mix the solid with four to six times as much anhydrous sodium carbonate and fuse the mixture in a platinum crucible. Cool, boil the residue with a little water until thoroughly disintegrated, and filter. Wash the residue with hot, normal sodium carbonate solution, until the filtrate gives no test for sulfate ions, and then with a little water. Dissolve the residue of barium carbonate in dilute hydrochloric, nitric, or acetic acid.

If the product of the fusion were treated with considerable water, or if the residue were washed at once with considerable hot water, the dissolved sodium sulfate would react with the insoluble barium carbonate to form less soluble barium sulfate. This is prevented, in accordance with the mass-action principle, by keeping the concentration of the sodium carbonate sufficiently large.

7. **Fluosilicic Acid** produces a white, crystalline precipitate of barium fluosilicate:

$$H_2SiF_6 + BaCl_2 \rightarrow 2\,HCl + BaSiF_6$$

In order to effect complete precipitation, the solution must stand some time. Barium fluosilicate is difficultly soluble in water and dilute acids, and insoluble in alcohol.

8. **Phosphates of the Alkalies:** same as with calcium.

9. **Sodium Phosphate** produces a white precipitate of barium phosphate, $BaHPO_4$, in neutral or alkaline solutions of barium salts as with calcium and strontium salts. According to Fresenius, $BaHPO_4$ is converted only partially into $Ba_3(PO_4)_2$ upon adding ammonium hydroxide.

10. **Sodium Rhodizonate,** $Na_2C_6O_6$. Place a drop of the neutral or acid solution to be tested upon filter paper and touch the wet spot with 1 drop of 5 per cent sodium rhodizonate solution. If no brown spot is formed, both Ba^{++} and Sr^{++} are absent. If a brown spot is formed touch it with dilute HCl; if Ba is present the spot turns red but the acid merely dissolves the brown spot caused by Sr.

11. **Sodium Sulfite** gives a white precipitate of barium sulfite, $BaSO_3$, which is not very soluble in dilute acetic or very dilute hydrochloric acid.

12. **Potassium Ferrocyanide** added to a concentrated solution of a barium salt gives a white, crystalline precipitate of barium potassium ferrocyanide, $BaK_2[Fe(CN)_6] \cdot 3\,H_2O$. In the presence of ammonium salts, the composition of the precipitate varies. The precipitate is more soluble than the corresponding calcium salt.

Reactions in the Dry Way

Heated with sodium carbonate on charcoal before the blowpipe, the barium compounds, unlike those of calcium and strontium, do not give a brightly luminous mass, because the barium carbonate formed is not decomposed at this temperature into the infusible oxide and carbon dioxide, but merely sinters together. Volatile barium salts color the non-luminous gas flame yellowish green. The sulfate is only slightly volatile in the hottest flame, and in the ordinary gas flame it shows scarcely any coloration. In order to obtain the coloration, it is best to change the sulfate into chloride, by reducing a small particle on a platinum wire in the upper reducing flame to sulfide. Then add a little hydrochloric acid by means of a capillary tube and hold in the flame which will now give the characteristic coloration.

Flame Spectrum.—A number of deep green lines, weaker lines in the orange-yellow part of the spectrum, and one blue line.

Orange-yellow (654.0 mμ, 629.8 mμ), (624.0 mμ, 617.9 mμ, 610.9 mμ, 603.2 mμ). Yellow 528.5, yellow triple line (576.9 mμ, 572 mμ, 564.8 mμ). Green 553.5 mμ, 534.7 mμ, 524.3 mμ, 513.7 mμ, 500.0 mμ. Blue 484.7 mμ.

MAGNESIUM, Mg. At. Wt. 24.32, At. No. 12

Density 1.75. M. P. 651°. B. P. 1380° ± 5°

Occurrence. — Magnesium compounds are found very abundantly in nature. The most important minerals are magnesite, $MgCO_3$, rhombohedral, isomorphous with calcite; dolomite, $(Ca,Mg)CO_3$; brucite, $Mg(OH)_2$, rhombohedral; carnallite, $KMgCl_3 \cdot 6\,H_2O$, orthorhombic; kieserite, $MgSO_4 \cdot H_2O$, monoclinic; epsomite, $MgSO_4 \cdot 7\,H_2O$, orthorhombic; spinel, $MgAl_2O_4$, isometric, isomorphous with magnetite, Fe_3O_4, and with chromite, $FeCr_2O_4$. Magnesium also occurs in a great many silicates. Thus almost all the minerals of the olivine group contain more or less magnesium. To this group belong forsterite, Mg_2SiO_4; monticellite, $CaMgSiO_4$; and olivine, $FeMgSiO_4$; all orthorhombic. An important decomposition product of the olivine minerals is serpentine, $Mg_3H_4Si_2O_9$. Almost all the minerals of the pyroxene-amphibole group, which are all related to orthorhombic enstatite, $MgSiO_3$, contain magnesium: augite, $MgAl_2SiO_6$; hornblende, an isomorphous mixture of $Mg_3CaSi_4O_{12}$ and 2 $(MgAl_2SiO_6)$; and tremolite, $CaMg_3Si_4O_{12}$, all three forming monoclinic crystals. Asbestos is a variety of tremolite with very fine fibers. Meerschaum is a magnesium silicate of the composition $H_4Mg_2Si_3O_{10}$, and is quite similar to talc, $H_2Mg_3Si_4O_{12}$, sometimes called steatite. Magnesium also occurs in the vegetable kingdom, being an essential constituent of the complex organic compound chlorophyll. In 1928 the world production of magnesite amounted to more than 800,000 metric tons, of which Austria produced nearly half.

Properties. — Magnesium is a silver-white metal, worth about 75 cents a pound. Its name is from *Magnesia*, a province in Thessaly. The metal is obtained by the electrolysis of molten, anhydrous magnesium chloride. This was first accomplished by Bussy in 1829. In 1929, more than a million pounds of the metal magnesium were produced. Alloyed with aluminum it is used a great deal when high tensile strength per unit of weight is desired, as in aircraft construction and for the beams of the delicate balances for chemical work. The carbonate has been used a great deal as an insulating material for covering steam pipes. Epsom salts, $MgSO_4 \cdot 7\,H_2O$, are valuable in medicine, more than 40,000 tons being produced in 1929.

Magnesium decomposes water very slowly, forming an oxide, MgO, which is only slightly soluble in water, forming magnesium hydroxide; the small quantity that dissolves is largely ionized, so that the solution has a faint alkaline reaction. Magnesium burns in the air giving a dazzling white light and forming the oxide. Magnesium reacts directly with nitrogen at 300° C, forming magnesium nitride (Mg_3N_2), which is readily decomposed by water, forming magnesium hydroxide and ammonia:

$$\mathbf{Mg_3N_2} + 6\,HOH \rightarrow 3\,\mathbf{Mg(OH)_2} + 2\,NH_3\uparrow$$

Almost all salts of magnesium are colorless and soluble in water and have a bitter taste. The solubility products of magnesium hydroxide, carbonate, phosphate, arsenate, and arsenite are so small that these substances may be regarded as insoluble. The sulfide, which can be prepared only in the dry way, is completely decomposed by water into hydroxide and hydrogen sulfide (hydrolysis). If an aqueous solution of magnesium chloride is evaporated to dryness on the water bath and the residual salt, $MgCl_2 \cdot 6\,H_2O$, is heated to 106° or higher, a basic salt insoluble in water is formed: $2\,MgCl_2 + H_2O \rightarrow \mathbf{Mg_2OCl_2} + 2\,HCl\uparrow$.

When a saturated solution of magnesium chloride is mixed with magnesium oxide, the mixture soon solidifies, forming a mass hard as stone, known as *magnesia cement*, consisting of basic magnesium chloride.

The elements manganese and magnesium, as their names indicate, were often confused in the early days of chemistry, and both were called magnesium. Thus the black oxide of manganese, MnO_2, was named *magnesia nigra*, and the white oxide of magnesium, MgO, was called *magnesia alba*. In many of their chemical properties, the two elements are similar. Manganese is characterized by forming compounds in several states of oxidation and is interesting for that reason, but magnesium is bivalent in all its stable compounds. Only one oxide is known with certainty, and from it all magnesium compounds are derived. This oxide, MgO, can be formed by burning the metal in the air or by heating the hydroxide, carbonate, sulfate, oxalate, etc. The hydroxide, $Mg(OH)_2$, is not appreciably soluble in water although aqueous suspensions are sold under the name *milk of magnesia*. Compared with the hydroxides of iron, aluminum, etc., magnesium hydroxide is much more soluble and it requires a higher concentration of OH^- ions to precipitate the hydroxide.

Reactions in the Wet Way

1. **Strong Bases,** such as the soluble hydroxides of sodium, potassium, and barium, precipitate white, gelatinous magnesium hydroxide; the precipitation is practically complete in the absence of ammonium salts or if the ammonium salt is all decomposed by boiling with an excess of the strong base (cf. p. 290):

$$Mg^{++} + 2\ OH^- \rightarrow \mathbf{Mg(OH)_2}$$

The solubility product of magnesium hydroxide (cf. p. 23) is about 1.2×10^{-11} at the laboratory temperature. The saturated solution of magnesium hydroxide in pure water contains about 0.000085 mole or 0.005 g $Mg(OH)_2$ per liter. In the presence of an excess of OH^-, the solubility of the magnesium hydroxide is much less, as a result of the common-ion effect (cf. p. 30), and it is possible, by keeping the volume of the solution small and using a slight excess of the reagent, to leave less than 1 mg of magnesium in solution.

The precipitation of magnesium hydroxide by means of the slightly ionized ammonium hydroxide can never be made complete, and if the solution already contains ammonium ions in sufficient excess, no precipitation of magnesium hydroxide takes place. Moreover, if a precipitate of magnesium hydroxide is boiled with a solution of an ammonium salt, such as ammonium chloride, the precipitate dissolves. This behavior is due to the fact that the ionization of ammonium hydroxide in the presence of ammonium salt (cf. pp. 50 and 290) is repressed to such an extent, as a result of the common-ion effect, that not enough OH^- ions are present at any one time to satisfy the solubility product of magnesium hydroxide, since the OH^- from the $Mg(OH)_2$ must be in equilibrium with the NH_4^+ ions from NH_4Cl.

Formerly, the incomplete precipitation of magnesium by ammonium hydroxide was explained by the assumption that complex salts such as $NH_4[MgCl_3]$ or $(NH_4)_2[MgCl_4]$ were formed, but this explanation has been discarded.* On the other hand, the fact that ammonium salts hinder the precipitation of magnesium ammonium phosphate and of the hydroxyquinolate does point to the formation of complex magnesium ions.

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* Cf. Loven, *Z. anorg. Chem.*, **11**, 404 (1896); Treadwell, *ibid.*, **37**, 326 (1903), and Herz, *ibid.*, **38**, 138 (1903).

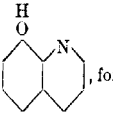
2. **Alkali Hypoiodite.** The following test, which will detect 0.3 γ of magnesium, depends upon the formation of a reddish brown, insoluble adsorption compound of $Mg(OH)_2$ and iodine. To 1 drop of neutral or acid solution to be tested on a white spot plate, add 1 tiny drop of N NaOH solution and 1 tiny drop of N I_2 solution. Stir with a glass rod, and after one minute add enough more NaOH to make the solution yellow (Feigl).

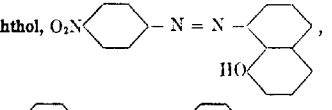
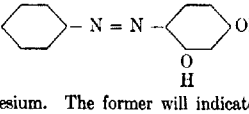
3. **Ammonium Carbonate** precipitates, in the absence of other ammonium salts, a basic salt (usually only on boiling or after long standing). The composition of the precipitated salt varies with the temperature and the concentration of the solution, the following salt being often obtained:

$$4\,Mg^{++} + 4\,(NH_4)_2CO_3 + H_2O \rightarrow \mathbf{Mg_4(CO_3)_3(OH)_2} + CO_2\uparrow + 8\,NH_4^+$$

The addition of an excess of ammonium carbonate reagent (p. 89) and an equal volume of 95 per cent alcohol causes the complete precipitation of magnesium as $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4\,H_2O$ from a cold, concentrated solution of magnesium salt.

The magnesium ammonium carbonate is fairly soluble in water, and the solubility increases rapidly with rise of temperature. Thus no precipitate is obtained upon the addition of ammonium carbonate to a hot dilute solution of magnesium salt containing ammonium chloride and no alcohol. (Note difference from barium, strontium, and calcium.)

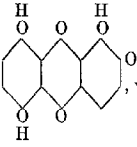
4. **8-Hydroxyquinoline,**  , for which the trivial name *oxine* has been proposed, precipitates magnesium completely from ammoniacal solutions which do not contain too much ammonium oxalate. The precipitate, $Mg(C_9H_6NO)_2$, is often recommended for the quantitative determination of magnesium. The precipitate can be weighed or it can be made to react with a known quantity of bromine and the excess determined by titration. One molecule of the precipitate reacts with 8 atoms of bromine.

5. ***p*-Nitrobenzene-azo-α-naphthol,**  , and ***p*-nitrobenzene-azo-resorcinol,**  , are very sensitive reagents for detecting magnesium. The former will indicate the presence of 0.19 γ of Mg^{++} in a single drop of solution, and the latter will indicate 0.5 γ of Mg^{++}. The reagents are prepared by dissolving 1 mg of the dyestuff in 100 ml of 2 N NaOH.

They will show the presence of magnesium in a single drop of tap water or in the ash of a qualitative filter paper. To carry out the test, mix 1 drop of the solution to be tested with 1–2 drops of reagent on a spot plate. According to the quantity of magnesium present, the reddish violet reagent will give a blue precipitate or a blue coloration. It is necessary to make sure that sufficient NaOH has been added; if the solution was too acid, the yellow color of the free dyestuff will appear. In testing for traces of magnesium it is necessary to compare the resulting color with that obtained in a blank test.

6. **Potassium Ferrocyanide** added to a cold solution gives a white precipitate of $K_2Mg[Fe(CN)_6]$. If NH_4^+ is present, $KNH_4Mg[Fe(CN)_6]$ is formed. If Rb^+ or Cs^+ is present the test is more delicate and Rb or Cs replaces K or NH_4 in the precipitate.

7. **Quinalizarin** (1, 2, 5, 8-tetrahydroxyanthraquinone),



, will detect in 1 drop of solution as little as 0.25 γ of magnesium. The test is carried out as follows: Take 1 drop of the solution to be tested on a spot plate, add 1 drop of water and mix with 2 drops of a solution containing 10–20 mg of quinalizarin in 100 ml of alcohol. If the solution is acid, the color of the mixture will be yellowish red. Add 2 *N* NaOH until the color changes to violet and enough more to increase the total volume 25–50 per cent. If magnesium is present a blue coloration or precipitate will be obtained. Compare the color with a blank test which should show a blue-violet color.

8. **Sodium Phosphate** is the most used reagent for magnesium. In solutions containing ammonium chloride, and in the presence of ammonia, it produces a white crystalline precipitate (orthorhombic, hemimorphous) of magnesium ammonium phosphate,

$$Mg^{++} + NH_4^+ + PO_4^{---} + 6\,H_2O \rightarrow \mathbf{MgNH_4PO_4 \cdot 6\,H_2O}$$

From very dilute solutions the precipitate separates only after standing some time, owing to the tendency to form supersaturated solutions. Rubbing the sides of the beaker with a glass rod hastens the formation of the precipitate.

The table on page 23 gives the solubility product of magnesium ammonium phosphate as 2.5×10^{-13}; about 0.0086 g of the salt dissolves in a liter of water at the laboratory temperature. The solubility in water is increased by its tendency to undergo hydrolysis:

$$MgNH_4PO_4 + HOH \rightleftarrows Mg^{++} + HPO_4^{--} + NH_4OH \qquad (I)$$

The tendency to undergo hydrolysis increases rapidly with rise in temperature (cf. p. 57). A similar decomposition is caused by hydrogen ions alone,

$$MgNH_4PO_4 + H^+ \rightleftarrows Mg^{++} + HPO_4^{--} + NH_4^+ \qquad (II)$$

which lessen the tendency for HPO_4^{--} to ionize; the precipitate, therefore, dissolves readily in the presence of any acid which is ionized more than HPO_4^{--}, even acetic acid (cf. p. 16). The presence of ammonium hydroxide prevents the hydrolysis, in accordance with the mass-action law. For this reason an excess of ammonium hydroxide is usually added. Ammonium chloride, by virtue of the common-ion effect, lessens the quantity of Mg^{++} ions required to reach the solubility product and causes reaction (II) to take place in the direction right to left; but, on the other hand, it should favor reaction (I) somewhat, because it represses the ionization of ammonium hydroxide. As a matter of fact, ammonium salts usually retard the formation of the precipitate, but do not eventually make it more soluble if an excess of ammonia is present.

Neubauer has shown that the conditions are still more complicated on account of the tendency for gelatinous $Mg_3(PO_4)_2$ and crystalline $Mg(NH_4)_4(PO_4)_2$ to form. Tri-magnesium phosphate, $Mg_3(PO_4)_2$, is formed in cold, strongly ammoniacal solutions containing but little ammonium salts. The monomagnesium tetrammonium phosphate is formed in neutral or slightly alkaline solutions containing considerable ammonium salts. B. Schmitz has shown that beautifully crystalline precipitates can be obtained in the presence of ammonium salts by adding sodium or ammonium phosphate to the boiling acid solution of the magnesium salt. Then, on adding 6 *N* ammonia equal to one-third the solution's volume and allowing the solution to cool, complete precipitation, as $MgNH_4PO_4 \cdot 6\,H_2O$, takes place.

9. **Titan Yellow A.** This dyestuff, $Na_2C_{28}H_{18}N_5S_4O_6$, is yellow in neutral aqueous or alcoholic solutions but brown in alkaline solutions. When adsorbed by $Mg(OH)_2$ a red color results which will serve to detect 1.5 γ of magnesium. To 1 drop of solution on a spot plate, add 1 drop of 0.1 per cent Titan Yellow A solution and mix with a little 0.1 *N* NaOH (Kolthoff, Feigl).

Reactions in the Dry Way

Mercuric Oxide heated with solid magnesium chloride converts it into magnesium oxide which does not dissolve appreciably in water. The mercuric chloride formed and the excess of mercuric oxide are volatilized.

All magnesium salts are more or less changed on heating in the air, leaving behind the oxide or an insoluble basic salt. On charcoal with sodium carbonate before the blowpipe, magnesium compounds are changed to white magnesium oxide, which is strongly luminous when hot. Calcium, strontium, and aluminum compounds behave the same way. The magnesium salts are non-volatile, do not color the flame, and give no flame spectrum, but do give a characteristic spark spectrum.

ANALYSIS OF GROUP IV

Separation of Calcium, Strontium, Barium and Magnesium

In the course of a systematic analysis calcium, strontium, and barium are always obtained in the form of their insoluble carbonates, either by precipitation with ammonium carbonate (cf. p. 261) or by fusion of the sulfates with sodium carbonate. Magnesium is not precipitated with the alkaline earth if the solution is dilute and contains considerable ammonium salt.

A number of excellent methods have been proposed for the analysis of the alkaline earth group. The characteristic reactions of barium, strontium, and calcium are so similar that difficulties are likely to arise in any scheme whenever a small quantity of one of these elements is present together with a large quantity of another; thus a precipitate caused by the presence of much strontium may be confused with one produced by a little barium. The method of analyzing the group to be described is that recommended by A. A. Noyes.

TABLE VI. — ANALYSIS OF GROUP IV

Solution may contain: Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, K^{+}, Na^{+}, NH_4^{+}. *Concentrate to 10 ml; add 15 ml $(NH_4)_2CO_3$ reagent, or more if necessary, and an equal volume of C_2H_5OH. Stir, let stand 30 minutes and filter. Test filtrate for Na^{+} and K^{+} according to Table* VII, *page* 295. *Dissolve the precipitate, which may contain $BaCO_3$, $SrCO_3$, $CaCO_3$, and $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4\ H_2O$, in 6-normal $HC_2H_3O_2$, and $NH_4C_2H_3O_2$ and K_2CrO_4.* (1)

Precipitate: $BaCrO_4$. *Dissolve in HCl. Evaporate to dryness. Test residue in flame, treat with 3 ml of 6-normal $HC_2H_3O_2$, 20 ml of 3-normal $NH_4C_2H_3O_2$, and 15 ml of water. Heat to boiling and test with K_2CrO_4 solution.* Yellow precipitate is $BaCrO_4$. (2)	Filtrate: Sr^{++}, Ca^{++}, Mg^{++}. *Add NH_4OH. Dilute to 65 ml and add 50 ml C_2H_5OH. Shake the solution with filter paper pulp and filter.* (3)		
	Precipitate: $SrCrO_4$. *Boil with $(NH_4)_2CO_3$ and $K_2C_2O_4$. Filter and reject the filtrate. Dissolve residue in 5 ml of normal $HC_2H_3O_2$ and add 2 ml of normal Na_2SO_4 solution.* White precipitate of $SrSO_4$ shows Sr is present. (4)	*Dilute with 50 ml of water, add 3 ml of 3-normal $K_2C_2O_4$. If a precipitate forms, add more $K_2C_2O_4$ if necessary, heat and filter.* (5)	
		Precipitate: CaC_2O_4. *Dissolve in 5 ml of 6-normal H_2SO_4 and add 20 drops of C_2H_5OH.* White precipitate is $CaSO_4$. (5)	Filtrate: Mg^{++}. *Add NH_4OH and Na_2HPO_4. Dissolve in 5 ml of 2-normal H_2SO_4, add 10 ml C_2H_5OH and filter if necessary. Add NH_4OH and Na_2HPO_4.* Precipitate is $MgNH_4PO_4$. (6)

PROCEDURE

1. Evaporate the filtrate from Group III in a casserole to complete dryness, upon a water bath toward the last to prevent bumping. Heat with a free flame until no more fumes are evolved. Cool, and if

perchloric acid has been used in the analysis, add 1 ml of 3 *N* NH_4Cl, evaporate, and ignite again. Cool, add 10 ml of water, and heat to boiling. Filter and to the cold filtrate add 15 ml of 6 *N* $(NH_4)_2CO_3$ reagent and 15 ml of C_2H_5OH. If a large precipitate results add 15 ml more of these two reagents. Shake well and allow to stand, with occasional shaking, for half an hour. Filter and wash with a little of the ammonium carbonate reagent. The filtrate contains the alkali ions and should be analyzed by the procedure for the analysis of Group VII, page 295.

Dissolve the precipitated carbonates by pouring small portions of hot acetic acid through the filter and evaporate the resulting solution to dryness without overheating the residue. Moisten the residue with 2 ml of 6-normal $HC_2H_3O_2$, 10 ml of 3-normal $NH_4C_2H_3O_2$, and 10 ml of water. Heat to boiling and precipitate the barium as chromate by adding hot 3-normal K_2CrO_4 solution, drop by drop, until no further precipitation takes place and the solution is decidedly yellow in color. Boil gently for about two minutes longer and filter through paper capable of holding very fine crystals.

2. If a considerable precipitate of strontium carbonate is obtained by the procedure given in § 3 below, it is possible that a *small* precipitate of chromate obtained in § 1 may be strontium chromate, and it is then necessary to try a confirmatory test for barium. Pour through the filter containing the chromate precipitate repeatedly, 5 ml of hot, 6-normal HCl and evaporate the solution just to dryness. Treat the residue with acetic acid, ammonium acetate, and potassium chromate solutions exactly as in § 1. If a yellow chromate precipitate is obtained again, barium is present.

3. To precipitate the strontium, add NH_4OH to the filtrate from § 1 till the color of the solution changes from orange to yellow and then add 5 ml more. Heat to about 65° and add 15 ml of alcohol in 5-ml portions, shaking fifteen seconds after each addition. Cool and allow to stand at least five minutes. If considerable strontium chromate is formed, add 5 ml more of potassium chromate solution and 15 ml of alcohol. Filter with suction but do not wash the precipitate. Place the filtrate aside for the calcium and magnesium tests (§ 5).

4. Pour repeatedly through the filter containing the strontium chromate precipitate a 10-ml portion of boiling-hot water. Add exactly 1 ml of 3-normal Na_2CO_3 solution and 12 ml of 3-normal $K_2C_2O_4$, and boil gently for five minutes in a covered casserole. Filter while hot and reject the filtrate. The precipitate will contain the strontium as carbonate, and any contaminating calcium will be present as oxalate. Wash the precipitate thoroughly with water and dissolve the carbonate

in 5 ml of cold, normal $HC_2H_3O_2$. To the solution add 2 ml of normal sodium sulfate solution, heat to boiling, and allow to stand ten minutes. A white precipitate of strontium sulfate shows the presence of strontium.

5. Dilute the ammoniacal filtrate from § 3 with 50 ml of water, add just 3 ml of 3-normal $K_2C_2O_4$ solution, and allow the mixture to stand at least fifteen minutes. If no precipitate of calcium oxalate is formed, pass on to § 6.

If a precipitate is obtained, heat the mixture to boiling and add 3–10 ml more of the $K_2C_2O_4$ reagent, according to the size of the carbonate precipitate obtained in § 1. Heat five minutes, filter, and wash with hot water. Test the filtrate for magnesium according to § 6. Treat the precipitate, or a small portion of it, with 5 ml of 6-normal H_2SO_4 to which 20 drops of alcohol have been added. Add 10 ml more of alcohol, and let the mixture stand for several minutes. A white precipitate of calcium sulfate shows the presence of calcium.

6. To test for magnesium ions, add 15 ml of 15-normal NH_4OH and 25 ml of normal Na_2HPO_4 to the filtrate from the $K_2C_2O_4$ treatment (§ 5). Cool, shake and allow to stand at least 30 minutes. Filter, reject the filtrate and wash the precipitate once with alcohol. To confirm the magnesium, dissolve the precipitate in 5 ml of 2 *N* sulfuric acid, add 20 ml of alcohol, and stir well for two or three minutes. Filter off any calcium sulfate that may form, and repeat the precipitation of the magnesium as phosphate (cf. p. 273).

COMPARATIVE SOLUBILITIES OF ALKALINE EARTH SALTS

The numbers in the table show the solubility in milliequivalents per liter at 20°. The letters v.s. (very soluble) denote more than 1 equivalent per liter.

	Mg	Ca	Sr	Ba
Sulfate	v.s.	30	1.5	0.02
Chromate	v.s.	60	12.	0.03
Carbonate	20.	0.2	0.2	0.2
Hydroxide	0.3	45.	130.	450.
Fluoride	3.8	0.4	1.9	18.
Oxalate	5.0	0.09	0.5	0.8

Quiz Questions

1. Make a table showing the relative soly. of the SO_4^{--}, CO_3^{--}, F^-, $C_2O_4^{--}$, and OH^- compds. with Ba, Mg, Ca, and Sr. In the table give the symbols of any chlorides or nitrates that are sol. in a mixt. of alc. and ether.

2. Starting with Ba^{++}, Ca^{++}, Sr^{++}, and Mg^{++}, outline the important chemical reactions that take place in the qual. anal. of this group, assuming that a pure ppt. is obtained in each case.

3. If a soln. contains 0.2748 g of Ba^{++} and 0.2629 g of Sr^{++}, how many ml of 3 *N* K_2CrO_4 will be necessary to combine with the Ba^{++} alone and how much to combine with both Ba^{++} and Sr^{++} and give 50 per cent in excess?

4. Show how by the reactions used in anal. it is easy to make pure $Ba(NO_3)_2$ from $BaCl_2$, pure KCl from K_2HPO_4, and $Ba(AcO)_2$ from $BaSO_4$. Give balanced chemical equations for all the reactions involved.

5. Why do we think that Na vapors are in the atmosphere of the sun? What sort of fireworks are made from $Sr(NO_3)_2$, $KClO_3$, and shellac, etc.?

6. Would NH_4HCO_3 be a suitable reagent for the alk. earth group? Explain carefully.

7. Explain why Sr is not pptd. when excess K_2CrO_4 is added to the HAcO soln. of Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++}.

8. What chemical changes take place when NH_4OH is added to the filtrate from the $BaCrO_4$ pptn.?

9. Write the chemical equations for the conversion of CrO_4^{--} ion into $HCrO_4^-$, and for the conversion of the $HCrO_4^-$ into $Cr_2O_7^{--}$.

Write the mass-action expression for the equilibrium in each of these reactions.

From these two expressions, deduce the mathematical relation between the H^+ concn. and the ratio of the CrO_4^{--} to $Cr_2O_7^{--}$ concns.

10. A soln. contains 200 mg of Ba and 300 mg of Sr. Without allowing for an excess of the reagent, how many ml of 3 *N* K_2CrO_4 would be necessary to yield the chromates of these elements?

GROUP V. THE ALKALI GROUP

POTASSIUM, SODIUM, AMMONIUM

The metals potassium and sodium are the most reactive of all the common positive elements (cf. p. 44). They oxidize very rapidly when exposed to the air and decompose water at ordinary temperatures; the hydrogen of water is reduced to the gaseous condition, and the metal is oxidized to alkali hydroxide in equilibrium with alkali cations and hydroxide anions. On account of the extent of their ionization (cf. p. 11) the alkali hydroxides form very strong bases. The solid hydroxides are the most stable of all hydroxides; they do not break down into oxide and water even on being melted. The pure oxides are difficult to prepare; cautious heating of the metals in air results in the formation of considerable peroxide as well as oxide.

The hydroxides of sodium and potassium can be prepared by dissolving the metal or the oxide in water, by adding alkaline earth oxide to a solution of alkali carbonate, or by the electrolysis of an aqueous solution of alkali chloride. The last method is the only one of industrial importance.

Sodium and potassium hydroxides are used as reagents in qualitative analysis. When added to solutions containing the soluble salts of cations of other analytical groups, insoluble hydroxide precipitates are formed except with arsenic, barium, strontium, and calcium. An excess of alkali hydroxide dissolves the amphoteric hydroxides of lead, antimony, tin, aluminum, and zinc.

Ammonium is classed with the alkali metals because the solubility of ammonium salts is similar to that of potassium salts. The ammonium radical differs from the alkali metals in being capable of oxidation, the usual product of the oxidation being nitrogen gas. Ammonium hydroxide is a much weaker base than the other hydroxides, and its salts are either volatile or are decomposed on being heated.

The salts of potassium, sodium, and ammonium are colorless for the most part, and readily soluble in water. Of these salts the carbonates, the tertiary and secondary phosphates, the cyanides, and the borates react alkaline in aqueous solution (hydrolysis). The salts of the alkalies are more or less volatile and impart characteristic colors to the nonluminous flame.

POTASSIUM, K. At. Wt. 39.096, At. No. 19

Density 0.862. M. P. 62.3°. B. P. 760°

The name potassium arises from the fact that potassium carbonate (potash) was one of the first potassium salts known and was found in the ashes formed by burning land plants. Potassium chloride and sulfate are important constituents of fertilizers. The German name for potassium is *Kalium*.

Occurrence. — Sylvite (KCl), isometric, and carnallite ($MgCl_2 \cdot KCl \cdot 6\,H_2O$) orthorhombic, occur at Stassfurt in the presence of halite and anhydrite; saltpeter (KNO_3), orthorhombic prisms; further, in very many silicates, *e.g.*, monoclinic feldspar ($KAlSi_3O_8$), and muscovite ($KH_2Al_3Si_3O_{12}$); also in plants in the form of organic salts, which on combustion yield potassium carbonate (potash). The annual world production of potassium salts corresponds to about 2,000,000 tons of K_2O, and of this enormous quantity about 70 per cent comes from Germany.

Preparation and Properties. — The element itself, which has no extensive commercial use, is prepared by the electrolysis of fused potassium chloride; it was first obtained by Davy in 1807. Next to cesium and rubidium, it has the greatest reduction potential of all metals. It oxidizes rapidly in moist air and is usually kept under kerosene. It decomposes water so violently that the hydrogen liberated burns with a violet flame, caused by small quantities of potassium vapors.

Oxide. — Potassium oxide can be prepared by carefully heating in a limited volume of air, but potassium peroxide, K_2O_4, is formed when potassium is heated in an excess of oxygen. The peroxide is a yellow powder and a powerful oxidizing agent.

Solubilities. — The metal and its oxides dissolve rapidly in water with liberation of considerable heat. Potassium also dissolves in alcohol, with evolution of hydrogen forming an alcoholate:

$$2\,C_2H_5OH + 2\,K \rightarrow 2\,C_2H_5OK + H_2$$

The carbonate and sulfate are insoluble in alcohol. Almost all potassium salts are dissolved by hot water: exceptions are some silicates and complex compounds in which the potassium is a minor constituent. To precipitate potassium salts from aqueous solutions, it is desirable to have the volume of the solution small and to keep it cold; usually it is necessary to add alcohol. The salts formed in precipitation reactions which can serve for the detection of potassium ions are the chloroplatinate, acid tartrate, fluosilicate, picrate, phosphomolybdate, perchlorate, periodate, fluotitanate, fluozirconate, silver cobaltinitrite, and the double salt with zirconium sulfate.

Reactions in the Wet Way

1. **Bismuth-Sodium Thiosulfate** (Carnot's* reaction). — If 1 drop of half-normal bismuth nitrate solution is mixed with 2 or 3 drops of half-normal thiosulfate solution and 10–15 ml of absolute alcohol (any turbidity being removed by the careful addition of a very little water), a sensitive reagent for potassium ions is prepared in which the bismuth is present in a complex anion:

$$Bi^{+++} + 3\,S_2O_3^{--} \rightarrow [Bi(S_2O_3)_3]^{---}$$

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* *Z. anal. Chem.* (**1897**), 512.

The sodium salt is soluble in alcohol but the yellow potassium salt is not:

$$Bi(S_2O_3)_3^{---} + 3\ K^+ \rightarrow \mathbf{K_3[Bi(S_2O_3)_3]}$$

The presence of ammonium chloride interferes with the test.

2. **Chloroplatinic Acid,*** $H_2[PtCl_6]$, gives in concentrated solutions of the chloride a yellow precipitate of potassium chloroplatinate,

$$PtCl_6^{--} + 2\ K^+ \rightarrow \mathbf{K_2[PtCl_6]}$$

which consists of small regular octahedra (visible with a magnifying glass). If the potassium solution is not very concentrated, no precipitation may appear at first; but on rubbing the inside of the beaker or test tube with a glass rod the formation of the precipitate will be hastened. NH_4^+, Cs^+, and Rb^+ ions give similar precipitates.

Whenever a crystalline precipitate is formed, the solution is supersaturated before the precipitate separates out, and the formation of crystals is hastened by the formation of small scratches on the sides of the beaker.

The behavior of the potassium chloroplatinate on ignition is characteristic; it is decomposed into chlorine, platinum, and potassium chloride:

$$K_2[PtCl_6] \rightarrow 2\ KCl + Pt + 2\ Cl_2\uparrow$$

If the products of ignition are treated with water, and the platinum filtered off, the filtrate will again give with chloroplatinic acid the yellow crystalline precipitate of $K_2[PtCl_6]$. (Note difference from ammonium chloroplatinate.)

Solubility of the Potassium Chloroplatinate in Water

One hundred ml of water dissolves at 0°, 0.70 g; at 10°, 0.90 g; at 20°, 1.12 g; and at 100°, 5.18 g $K_2[PtCl_6]$.

In a saturated KCl solution, or in 75 per cent alcohol, the precipitate is practically insoluble.

For this reaction it is best to use the chloride. The addition of chloroplatinic acid to potassium iodide solution causes a deep reddish brown color due to the conversion of $[PtCl_6]^{--}$ into $[PtI_6]^{--}$ ion, of which the potassium salt is more soluble:

$$[PtCl_6]^{--} + 6\ I^- \rightarrow [PtI_6]^{--} + 6\ Cl^-$$

Similarly, potassium cyanide is not precipitated by chloroplatinic acid, owing to the formation of complex platinum-cyanogen compounds.

To test an iodide or cyanide for potassium, the salt should first be changed to chloride by evaporation with concentrated hydrochloric acid.

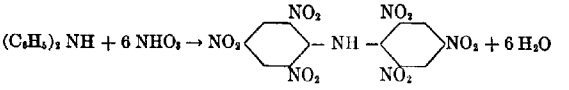
3. ***p*-Dipicrylamine.†** If diphenylamine is dissolved in concentrated sulfuric acid

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* Platinic chloride, $PtCl_4$, gives no precipitate with potassium salts, or at least only after long standing. The above reagent, chloroplatinic acid, is a dibasic acid and is obtained by dissolving platinum in aqua regia. The solution is prepared of such strength that there are 10 g of platinum in every 100 ml.

† N. S. Poluektov, *Mikrochemie*, **14**, 265 (1933-34).

and this solution is introduced into fuming nitric acid, hexanitrodiphenylamine (*p*-dipicrylamine) is formed:



After the stormy reaction has abated, heat the reaction mixture gently to complete the nitration. Pour into ice water, filter, and wash until free from acid. Recrystallize from glacial acetic acid. As reagent dissolve 0.2 g of the yellow dyestuff (m.p. 234°) in 2 ml of *N* Na_2CO_3 and 20 ml of water; heat to boiling, and filter. The sodium salt of *p*-dipicrylamine dissolves in water to a yellow solution, which gives with K^+ an orange-red, finely crystalline precipitate. Rubidium, cesium, and considerable ammonium give similar precipitates. The test can be obtained on filter paper with 3 γ of K^+ in the presence of 10,000 times as much solution.

4. **Fluosilicic Acid,** H_2SiF_6, added in considerable excess to a solution of a potassium salt, precipitates gelatinous potassium fluosilicate,

$$SiF_6^{--} + 2\,K^+ \rightarrow \mathbf{K_2SiF_6}$$

which is difficultly soluble in water and dilute acids and insoluble in alcohol. On heating, it is decomposed into volatile silicon fluoride, and potassium fluoride remains behind:

$$\mathbf{K_2SiF_6} \rightarrow 2\,\mathbf{KF} + SiF_4\uparrow$$

The solution must not be alkaline; the fluosilicate ion decomposes and silicic acid precipitates:

$$[SiF_6]^{--} + 4\,OH^- \rightarrow \mathbf{Si(OH)_4} + 6\,F^-$$

5. **Perchloric Acid,** $HClO_4$, precipitates white, crystalline potassium perchlorate:

$$HClO_4 + K^+ \rightarrow H^+ + \mathbf{KClO_4}$$

100 ml of water at 0° dissolves 0.75 g, and at 100° 19.8 g of $KClO_4$. It is so slightly soluble in 97 per cent alcohol that the precipitate can be obtained with less than 2 mg of potassium ions.

A dangerous explosion will result if the alcoholic solution is heated and the vapors take fire.

6. The reagents used in testing for alkaloids — **picric acid** or **sodium picrate, sodium phosphotungstate,** and **phosphomolybdic acid** — give precipitates with potassium salts. With picric acid and phosphomolybdic acid the precipitates are yellow, but the precipitate produced by phosphotungstic acid is white.

7. **Sodium Cobaltinitrite,** $Na_3[Co(NO_2)_6]$, precipitates yellow potassium-sodium cobaltinitrite from neutral or slightly acid solution:

$$Na_3[Co(NO_2)_6] + 2\,KCl \rightarrow \mathbf{K_2Na[Co(NO_2)_6]} + 2\,NaCl$$

Similar precipitates are obtained with NH_4^+, Rb^+ and Cs^+. The test must not be made in an alkaline solution or $Co(OH)_3$ will precipitate. If the reagent is prepared as recommended by Biilmann,* as little as 0.0009 mg (0.9 γ) can be detected in the presence of 4,000 equivalents of Na. Since $K_2Ag[Co(NO_2)_6]$ is less soluble than $K_2Na[Co(NO_2)_6]$ the following procedure is recommended for detecting 1 γ of potassium in the absence of halide: Place 1 drop of the neutral or acetic acid solution on a black spot plate together with a drop of 0.05 per cent $AgNO_3$ reagent and a little solid $Na_3[Co(NO_2)_6]$ (Burgess and Kamm, Feigl).

8. **Tartaric Acid,** $H_2C_4H_4O_6$, produces, in not too dilute neutral solutions of potassium salts, a white crystalline precipitate of potassium acid tartrate (orthorhombic, hemihedral):

$$K^+ + H_2C_4H_4O_6 \rightarrow KHC_4H_4O_6 + H^+$$

Rubbing the inside walls of the dish will hasten the formation of the precipitate. Potassium acid tartrate is readily soluble in mineral acids, but difficultly soluble in acetic acid and water; 100 ml of water at 10° C dissolves 0.425 g of this salt. The addition of a little sodium acetate increases the sensitivity of this test, but too much is harmful. The precipitate dissolves in hot water and in dilute solutions of caustic alkalies and ammonia. Potassium acid tartrate is an important constituent of many baking powders; it is called *cream of tartar*. Upon ignition potassium carbonate and carbon are formed and empyreumatic vapors (odor of burnt sugar) are given off.

9. **Zirconium Sulfate,** $Zr(SO_4)_2$, in concentrated, aqueous solutions precipitates a double sulfate even in the presence of considerable sodium, ammonium, lithium, rubidium, and cesium ions. One milligram of potassium can be detected in 2 ml of solution. (See Reed and Withrow, *J. Am. Chem. Soc.*, **51**, 1062 (1929).) Potassium fluorzirconate, K_2ZrF_6, is another difficultly soluble salt; 100 ml of water dissolves about 1.5 g at room temperature.

Reactions in the Dry Way

Potassium compounds color the non-luminous flame violet. The presence of very small amounts of sodium obscures the violet color, but if the flame is viewed through cobalt glass or indigo solution, the reddish violet potassium rays pass through, while the yellow sodium rays are completely absorbed.

Flame Spectrum. — Potassium gives a characteristic flame spectrum. A double red line, 769.9 mμ and 766.5 mμ (appearing as a single line with weaker dispersion), and a faint violet line, 404.4 mμ, appear at comparatively low temperatures. With a hotter flame, other lines are visible in the yellow, 583.2 mμ, 580.2 mμ, and 578.2 mμ; and in the green, 535.1 mμ and 511.3 mμ.

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* *Z. anal. Chem.*, **39**, 284 (1900).

SODIUM, Na. At. Wt. 22.997, At. No. 11

Density 0.97. M. P. 95.6°. B. P. 882.9°

Sodium (natrium) is a silvery white metal with metallic luster when not coated with oxide by exposure to air. It is a good conductor of heat. It oxidizes rapidly in moist air and hence is kept under benzene or kerosene. It decomposes water but not as violently as potassium does; the liberated hydrogen gas sometimes takes fire. It burns at a red heat with a yellow flame. The name sodium is derived from soda (Na_2CO_3), one of its first known salts.

Occurrence. — Sodium occurs very extensively in nature. Its most important mineral is halite, or rock salt (NaCl), isometric system. Halite is found in very large deposits, often quite pure, but usually contaminated with clay, anhydrite, and gypsum. Dissolved sodium chloride is present in large amounts in the ocean and in many salt springs. Sodium also occurs in nature in the form of carbonate, as thermonatrite ($Na_2CO_3 \cdot H_2O$), orthorhombic; natron or soda ($Na_2CO_3 \cdot 10\,H_2O$), monoclinic; trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2\,H_2O$), monoclinic; as nitrate in Chile saltpeter, or soda niter ($NaNO_3$), hexagonal, rhombohedral; as cryolite (Na_3AlF_6), triclinic; in many silicates as albite ($NaAlSi_3O_8$), triclinic; and as tinkal, borax ($Na_2B_4O_7 \cdot 10\,H_2O$), monoclinic. The annual production of sodium chloride is more than 7,500,000 tons and of sodium nitrate more than 3,000,000 tons.

Oxides and Hydroxide. — When sodium burns in oxygen, the peroxide, Na_2O_2, is formed, which is changed to sodium oxide, Na_2O, by heating again with sodium. The white monoxide is very hygroscopic. Heating to above 400° changes Na_2O back to Na_2O_2 and Na. Sodium peroxide is an excellent oxidizing agent. It dissolves in water to form NaOH and O_2, and in acids to form sodium salt and hydrogen peroxide. Some hydrogen peroxide is formed when sodium peroxide is dissolved in cold water, but this is not stable and decomposes completely by heating the alkaline solution. Hydrogen peroxide is stable in acid solutions. The hydroxide, like potassium hydroxide, is best formed by the electrolysis of the chloride in aqueous solution, but it can also be prepared by dissolving either oxide in water, or by treating sodium carbonate solution with alkaline earth oxide and filtering off the insoluble alkaline earth carbonate that results.

Sodium peroxide, sodium hydroxide, sodium carbonate, and other sodium salts are much used as reagents in qualitative analysis. They behave like the corresponding potassium salts. Most sodium salts are easily dissolved by water. Sodium chloride is only slightly soluble in water which is saturated with HCl, and then upon adding alcohol the precipitation of NaCl is complete.

Sodium antimonate, the triple acetates of sodium and uranium with zinc, magnesium, or cobalt, and the triple nitrite of sodium, cesium, and bismuth are the most useful precipitates for the detection of sodium.

Reactions in the Wet Way

1. **Ball's Reagent.** — A solution of bismuth and cesium *nitrites* in dilute nitric acid gives a precipitate corresponding to the formula $6\,NaNO_2 \cdot 9\,CsNO_2 \cdot 5\,Bi(NO_2)_3$. Tschopp* has used this reaction for the micro determination of small quantities of sodium.

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* *Helv. Chim. Acta*, 8, 893 (1925).

To prepare the reagent, place 30 g of pure KNO_3 in a 100-ml flask, dissolve it in about 60 ml of water, and add a solution of 3 g of $Bi(NO_3)_3 \cdot 5\,H_2O$ in just enough dilute nitric acid to prevent precipitation of basic bismuth salt. Add an aqueous solution of 1.6 g of $CsNO_2$ and dilute the mixture to 100 ml. After allowing it to stand over night, filter. To detect small quantities of sodium, add to the concentrated solution to be tested, 3 ml of the well-cooled reagent for each milligram of sodium probably present, shake the mixture, stopper the container, and allow to remain in an ice chest over night.

2. **Hydrochloric Acid** and **Alcohol** precipitate sodium chloride. If dry hydrogen chloride is passed into 100 ml of an alcoholic solution of a sodium salt, less than 1 mg of sodium will remain in solution.

3. **Magnesium uranyl acetate,** added to not more than 5 ml of aqueous solution, precipitates 5–50 mg of sodium completely as greenish yellow $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 6\frac{1}{2}\,H_2O$. Noyes and Bray* add 1 ml of alcohol and 5 ml of reagent to 5 ml of aqueous solution; 0.5 mg of sodium gives a precipitate, but 2 mg of lithium or 10 mg of NH_4, K, Rb, or Cs do not interfere. According to Feigl, 12.5 γ of sodium can be detected.

Caley and Foulk† do not add alcohol but use 100 ml of reagent when 10 mg or less of sodium is present. Instead of using magnesium acetate in the reagent, zinc acetate‡ or cobalt acetate§ has been suggested.

4. **The Oxalate Ion.** — Sodium oxalate, $Na_2C_2O_4$, is much less soluble in water and in dilute alcohol than are the corresponding potassium and ammonium salts. To test for sodium, L. W. Winkler‖ recommends adding a saturated solution of $K_2C_2O_4$ and some alcohol. Meyerfield¶ recommends a saturated solution of ammonium oxalate, while Schoorl** shakes 0.5 g of the solid to be tested for sodium with 2.5 ml of 20 per cent potassium oxalate solution.

5. **Potassium Antimonate,** KH_2SbO_4,†† produces in neutral or weakly alkaline solutions of sodium salts a heavy, white crystalline precipitate, which is formed more quickly by rubbing the inside walls of the vessel with a glass rod:

$$KH_2SbO_4 + Na^+ \rightarrow NaH_2SbO_4 + K^+$$

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* *Qualitative Analysis for the Rare Elements.*

† *J. Am. Chem. Soc.*, **51**, 1664 (1929).

‡ Kolthoff, *Z. anal. Chem.*, **70**, 397 (1927).

§ Caley, *J. Am. Chem. Soc.*, **51**, 1965 (1929).

‖ *Pharm. Zentralhalle*, **66**, 669 (1925).

¶ *Z. anal. Chem.*, **67**, 150 (1925).

** *Pharm. Weekblad*, **63**, 555 (1926).

†† This reagent was formerly called potassium pyroantimonate. Note that $K_2H_2Sb_2O_7 \cdot H_2O$ is the same as $2\,KH_2SbO_4$.

The test must not be made in acid solution for then an amorphous precipitate of antimonic acid will be obtained. Ammonium salts of strong acids are likely to give an amorphous precipitate on standing: acid is formed by the hydrolysis of the ammonium salt and antimonic acid is precipitated. No metals other than the alkalies should be present because they also give precipitates with antimonic acid, amorphous ones as a rule.

6. **Tartaric Acid** and **Chloroplatinic Acid** do not precipitate sodium salts, the sodium salts of these acids being soluble in alcohol as well as in water. (Note difference from potassium.) Sodium chloroplatinate is orange in color.

Sodium Peroxide, Na_2O_2

This substance, which is now used commercially on account of its energetic oxidizing power, is obtained as a heavy yellow powder by burning dry sodium in the air. It shows the following characteristic reactions:

Behavior toward Water. — If a little water is added to some of this substance in a test tube, considerable heat is evolved and oxygen gas is liberated (sufficient to ignite a glowing splinter).* Water decomposes the sodium peroxide, according to the equation:

$$Na_2O_2 + 2\,H_2O \rightarrow 2\,NaOH + H_2O_2$$

But on account of the heat of the reaction a part of the hydrogen peroxide is decomposed into water and oxygen, $2\,H_2O_2 \rightarrow 2\,H_2O + O_2\uparrow$.

If the solution is kept cold, which can be done by throwing the sodium peroxide in small portions into ice water it will dissolve, with scarcely any evolution of oxygen, to a clear, strongly alkaline liquid, which gives, as before, all the reactions of hydrogen peroxide.

If some sodium peroxide is placed on a watch glass under a bell jar and near an evaporating-dish containing water, the sodium peroxide in twelve hours will completely change over to a pure white hydrate ($Na_2O_2 \cdot 8\,H_2O$), which will dissolve in water without decomposition at the ordinary temperature. By standing in a desiccator over sulfuric acid, the octahydrate is changed to $Na_2O_2 \cdot 2\,H_2O$.

Hydrogen Peroxide, H_2O_2

(*a*) *In Acid Solution*

If the solution obtained by the action of water on sodium peroxide is used for these tests, it must be acidified with dilute sulfuric acid, care being taken to keep the solution cool.

1. **Chromic Acid.** — If the acid solution of hydrogen peroxide is shaken with a little ether (free from alcohol) and a trace of potassium dichromate is added, after which the mixture is again shaken, the

* This will sometimes cause an explosion. Commercial sodium peroxide often contains metallic sodium, which with water forms hydrogen; thus both hydrogen and oxygen are set free at the same time, and the glowing splinter may then cause an explosion. (Private communication from E. Constam.)

upper layer of ethereal solution will be colored a beautiful blue, owing to the formation of chromium peroxide (cf. p. 202).

This test is very sensitive and will detect as little as 0.1 mg of H_2O_2. In carrying out this test, a *blank* test must always be tried with the ether alone, because, after standing in the air, it is likely to contain some ethyl peroxide $(C_2H_5)_4O_3$ (?), which gives the test. It is possible to free the ether from this peroxide by letting it stand over night in contact with sodium and then redistilling it. It must not be distilled before treating with sodium since an explosion is likely to occur.

2. **Permanganic Acid** in acid solution will be decolorized, with evolution of oxygen:

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,O_2\uparrow$$

Similar to the permanganate, many other oxides are reduced by hydrogen peroxide, with evolution of oxygen; *e.g.*, Ag_2O, Pb_3O_4, PbO_2, MnO_2, Co_2O_3, etc.:

$$Ag_2O + H_2O_2 \rightarrow H_2O + O_2\uparrow + 2\,Ag$$

$$MnO_2 + H_2O_2 + 2\,H^+ \rightarrow Mn^{++} + 2\,H_2O + O_2\uparrow$$

$$Co_2O_3 + H_2O_2 + 4\,H^+ \rightarrow 2\,Co^{++} + 3\,H_2O + O_2\uparrow$$

3. **Potassium Ferricyanide** and **Ferric Chloride.** — If a trace of potassium ferricyanide is added to a very dilute and nearly neutral solution of ferric chloride, so that the solution appears a distinct yellow, and a nearly neutral solution of hydrogen peroxide is then added, the mixture will soon assume a green tint, and finally, on standing, Prussian blue will separate out. The potassium ferricyanide is reduced by the hydrogen peroxide to potassium ferrocyanide, which forms Prussian blue with the ferric chloride:

$$2\,[Fe(CN)_6]^{---} + H_2O_2 \rightarrow 2\,[Fe(CN)_6]^{----} + O_2\uparrow + 2\,H^+$$

and

$$3\,[Fe(CN)_6]^{----} + 4\,Fe^{+++} \rightarrow Fe_4[Fe(CN)_6]_3$$

According to Schönbein, as little as 0.02 mg H_2O_2 per liter may be detected by this reaction. Since many other substances ($SnCl_2$, SO_2, etc.) will reduce potassium ferricyanide to potassium ferrocyanide, this reaction alone is not always a reliable test.

4. **Starch Paste** and **Potassium Iodide.** — If to an acid solution containing starch paste and potassium iodide some hydrogen peroxide is added, a blue color will at once appear:

$$2\,KI + H_2O_2 \rightarrow 2\,KOH + I_2$$

By means of this reaction, 0.05 mg per liter of hydrogen peroxide may be detected.

5. **Titanium Sulfate** gives a distinct yellow color, caused by the formation of pertitanic acid, $Ti^{++++} + H_2O_2 + 2\,H_2O \rightarrow 4\,H^+ + H_2TiO_4$. Some chemists prefer to write the formula of pertitanic acid as $TiO_2 \cdot H_2O_2$, which assumes a true peroxide structure instead of sexivalent titanium.

This is the most delicate test for hydrogen peroxide. The titanium sulfate solution for this reaction may be prepared by fusing titanium dioxide with 15–20 parts of potassium pyrosulfate and dissolving the fusion in cold, dilute sulfuric acid. It may also be prepared by heating titanium dioxide with concentrated sulfuric acid, cooling, and diluting carefully.

The addition of alkali hydroxide, ammonia, or ammonium carbonate to an acid solution of pertitanic acid gives a yellowish orange precipitate which redissolves in an excess of the alkaline reagent. Classen has used this reaction as a method for separating titanium from ferric iron.*

(*b*) *In Alkaline Solution*

1. **Gold Chloride** will be reduced to metal by hydrogen peroxide at ordinary temperatures with evolution of oxygen. The gold usually separates in a very finely divided state, and appears brown by reflected light and greenish blue by transmitted light:

$$2\,Au^{+++} + 3\,H_2O_2 + 6\,OH^- \rightarrow 2\,Au + 6\,H_2O + 3\,O_2\uparrow$$

If very dilute gold solutions are used, the metal sometimes separates out in the form of a yellowish film adhering to the sides of the test tube.

2. **Salts of Manganese** and **Cobalt** give dark-colored precipitates:

$$Mn^{++} + 2\,OH^- + H_2O_2 \rightarrow H_2O + \underset{\text{Brown}}{MnO(OH)_2}$$

$$2\,Co^{++} + 4\,OH^- + H_2O_2 \rightarrow 2\,\underset{\text{Black}}{Co(OH)_3}$$

Hypochlorites give the same reactions with manganese and cobalt salts, but they do not give the reaction with gold chloride.

Ozone, O_3

Ozone is always formed when oxygen is exposed to the silent electric discharge. It is often present in oxygen that has been prepared electrolytically and, according to Brunck, is present to some extent in the gas prepared by ignition of potassium chlorate. Ozone is a strong oxidizing agent and behaves in many respects like hydrogen

* *Ber.*, **21**, 370 (1888).

peroxide, with which it is often confused. Ozone may be distinguished from hydrogen peroxide as follows:

1. Ozone does not give a yellow coloration with titanium sulfate solution.
2. Ozone does not cause precipitation of gold from its solutions.
3. Ozone sets free iodine immediately from dilute, neutral potassium iodide solution.
4. Ozone liberates bromine from an acid solution of sodium bromide.
5. Ozone causes bright metallic silver at once to assume a steel-blue tint.

The sensitiveness of this last reaction is remarkable if carried out according to the directions of Manchot and Kampeschulte. Heat a bright piece of silver foil to about 240° and then expose it to the action of ozone; steel-blue spots with violet edges at once appear. This reaction does not usually take place with pure silver in the cold. If, however, the silver is polished by rubbing with emery paper, the reaction will then take place in the cold. Traces of iron oxide are left upon the silver from the emery and catalyze the reaction. Other oxides, Ag_2O, CoO, NiO, Bi_2O_3, Pb_3O_4, V_2O_5, MnO_2, CuO, ThO_2, CeO_2, TiO_2, WO_3, U_3O_8, and to a less degree MoO_3, HgO, CaO, and BaO, have a similar effect. Thus if the silver is etched with nitric acid and is then dried, it will react with ozone in the cold.

Reactions in the Dry Way

Sodium salt vapors color the non-luminous gas flame a monochromatic yellow, which can be readily distinguished from the yellow flame of the gas in the following way: If we illuminate an orange-colored body (such as a stick of sealing wax or a crystal of potassium dichromate) with white light (all glowing solid bodies emit white light), the red and orange rays will be reflected: the body appears orange. If these bodies are illuminated with the monochromatic sodium light, they can now only reflect yellow light: the bodies appear yellow (a delicate test).

Flame Spectrum.—A yellow double line (589.6 mμ and 587.0 mμ, coinciding with the D-line of the sun's spectrum. This is an extremely delicate reaction; 1×10^{-7} mg of sodium can be recognized in the spectrum.

AMMONIUM, NH_4

Occurrence.—In small amounts as carbonate and nitrite in the air; as ammonium chloride in the fissures of active volcanoes. Ammonium derivatives are formed by the decay of many organic substances containing nitrogen: albumin, urea, etc.,

$$CO(NH_2)_2 + H_2O \rightarrow CO_2\uparrow + 2\ NH_3\uparrow$$

and in a similar way by the dry distillation of many nitrogenous substances, such as coal, horn, hair, etc.

The name ammonium is probably derived from the Greek *Ammos* = sand. Possibly the name is related to the ancient temple of Jupiter called *Ammon*.

Although ammonium itself is known only in the form of its amalgam, we are justified in considering it at this place because the aqueous solutions of ammonium salts

react with reagents as if they contained a cation of a metal resembling potassium, and ammonium salts are isomorphous with potassium salts.

Ammonia, NH_3, can be condensed to a liquid at $-34°$ and to a solid at $-79°$. At 25°, NH_3 has a vapor pressure of 9.9 atmospheres and burns in oxygen without heating. It combines energetically with acids to form salts of the univalent ammonium ion. At 0°, one volume of water absorbs 1,300 volumes of NH_3, and 700 volumes at 20°. The aqueous solution acts as a precipitant like the hydroxides of sodium and potassium. It throws out certain hydroxides as insoluble precipitates, but many hydroxides precipitated by sodium hydroxide are not formed on adding ammonia partly because of the slight extent to which hydroxide ions are present and partly because of the tendency of NH_3 to form complex ions with many cations. Thus the hydroxides of silver, copper, cadmium, nickel, cobalt, and zinc are dissolved by ammonia water because of the formation of soluble ammoniate ions, *e.g.*, $Cu(NH_3)_4^{++}$ and magnesium hydroxide is not precipitated by ammonia in the presence of considerable NH_4 salt, although almost entirely precipitated by sodium hydroxide, because the NH_4^+ salt represses the ionization of NH_4OH to an extent such that the solubility product of $Mg(OH)_2$ is not reached.

Ammonia is made synthetically by the interaction of nitrogen and hydrogen in the presence of a catalyst (Haber process, Claude process) and by the reaction of cyanamide ($CaCN_2$ from CaC_2 heated in N_2) with steam. Ammonia is also obtained as a by-product in the coking of coal.

Reactions in the Wet Way

1. **Strong bases,** NaOH, KOH or $Ca(OH)_2$, added to an ammonium salt in the presence of a little water cause the evolution of ammonia on heating; the gas can be recognized by its odor, by fumes of ammonium chloride being formed when a rod moistened with 12 *N* hydrochloric acid is placed in contact with the vapors, by its turning red litmus blue, or by the blackening of mercurous nitrate paper:

$$2\,Hg_2(NO_3)_2 + 4\,NH_3 + H_2O \rightarrow 3\,NH_4NO_3 + O\begin{matrix}\diagup\,Hg\,\diagdown \\ \diagdown\,Hg\,\diagup\end{matrix}NH_2\cdot NO_3 + 2\,Hg$$

Black

The reaction of strong bases upon ammonium salts may be explained on the basis of the laws of chemical equilibrium. Ammonia, NH_3, is a gas which is very soluble in cold water and insoluble in boiling water; at 100° all the gas can be expelled, and there is no constant-boiling mixture as in the case of hydrochloric acid (pp. 69, 299).

The solution of ammonia in water at the laboratory temperature is in a state of equilibrium

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

and, for this equilibrium, the mass-action expression (p. 17) is

$$\frac{[NH_4^+] \times [OH^-]}{[NH_3]} = k = 1.8 \times 10^{-5}$$

The ammonium salts, unlike the free base, are largely ionized. When, therefore, an excess of OH^- is added to the solution of an ammonium salt, it is necessary, in order to establish equilibrium between NH_4^+ and OH^-, for the greater part of the

NH_4^+ to be converted into NH_4OH, and then, to establish equilibrium between NH_4OH and NH_3, about two-thirds of the NH_4OH is changed into NH_3. By boiling the solution, the NH_3 is expelled and the above-mentioned states of equilibrium are disturbed and, as the final result, all the original NH_4^+ becomes converted into NH_3 gas. Less than 0.2 mg of ammonium can be detected by the litmus test when properly carried out. Care should be taken not to boil the solution so that some of the alkaline liquid becomes spattered into the nostril or upon the test paper.

Certain complex ammonia derivatives do not always evolve ammonia in this test. When pure mercuric aminochloride, $Hg\begin{matrix}\diagup NH_2\\ \diagdown Cl\end{matrix}$, is heated with caustic soda solution, a part of the nitrogen is evolved as ammonia, but if considerable mercuric salt is present the test is not obtained. This is because the mercuric aminochloride itself is only slightly soluble in water and, especially in the presence of an excess of mercuric compounds, furnishes scarcely any ammonium ions. If some potassium sulfide is added, however, the mercury is converted into more insoluble mercuric sulfide and the ammonia test can be obtained:

$$\mathbf{Hg}\begin{matrix}\diagup \mathbf{NH_2}\\ \diagdown \mathbf{Cl}\end{matrix} + K_2S + H_2O \rightarrow \mathbf{HgS} + KCl + KOH + NH_3\uparrow$$

Water itself in some cases causes evolution of ammonia gas. It decomposes many nitrides, metal amides and cyanamides:

$$Mg_3N_2 + 6\,HOH \rightarrow 3\,\mathbf{Mg(OH)_2} + 2\,NH_3\uparrow$$

$$NH_2Na + HOH \rightarrow NaOH + NH_3\uparrow$$

$$\underset{\text{Calcium cyanamide}}{CaCN_2} + 3\,H_2O = \mathbf{CaCO_3} + 2\,NH_3\uparrow \text{ (at high temperatures)}$$

2. **Chloroplatinic Acid** gives a yellow crystalline precipitate:

$$H_2[PtCl_6] + 2\,NH_4^+ \rightarrow \mathbf{(NH_4)_2[PtCl_6]} + 2\,H^+$$

This salt may be distinguished from the potassium salt —

(*a*) by its behavior on ignition; platinum alone is left behind:

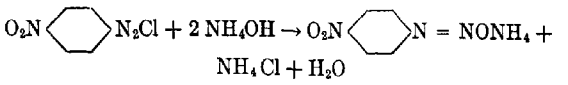
$$3\,\mathbf{(NH_4)_2[PtCl_6]} \rightarrow 2\,N_2\uparrow + 2\,NH_3\uparrow + 18\,HCl\uparrow + 3\,\mathbf{Pt}$$

(*b*) by its behavior on treating with strong bases, whereby the smell of ammonia may be detected:

$$\mathbf{(NH_4)_2[PtCl_6]} + 2\,NaOH \rightarrow Na_2[PtCl_6] + 2\,H_2O + 2\,NH_3\uparrow$$

3. **Paranitrodiazobenzene** solution in the presence of alkali gives a reddish yellow, flocculent precipitate, and the solution becomes yellow or red. The reaction depends upon the formation of an ammonium

salt of *p*-nitrophenylnitrosamine,*



$$O_2N\langle\bigcirc\rangle N_2Cl + 2\,NH_4OH \rightarrow O_2N\langle\bigcirc\rangle N = NONH_4 + NH_4Cl + H_2O$$

Less than 1γ of NH_3 can be detected by this test.

4. **Picric Acid, Sodium Tungstate,** and **Phosphomolybdic Acid** give precipitates as with potassium ions. Perchloric acid and potassium antimonate do not give precipitates.

5. **Potassium Iodide** and **Sodium Hypochlorite** solutions cause the precipitation of black nitrogen iodide:

$$2\,NH_4^+ + 2\,I^- + 2\,ClO^- \rightarrow \mathbf{NHI_2} + NH_3 + 2\,Cl^- + 2\,H_2O$$

To make the test, which is a sensitive one, the neutral or alkaline solution of the ammonium salt is treated with a few drops of 10 per cent potassium iodide and a drop of saturated sodium hypochlorite solution.

6. **Sodium Cobaltinitrite** gives a yellow precipitate similar to that produced with potassium. Before testing for potassium with this reagent, therefore, it is necessary to expel ammonium salts by evaporating the solution to dryness in a porcelain dish and heating until no more fumes are evolved. Small quantities of ammonium salts can be removed by boiling with a little sodium nitrite and acetic acid:

$$NH_4^+ + NO_2^- \rightarrow N_2\uparrow + 2\,H_2O$$

7. **Tartaric Acid** produces, as with potassium, a white, crystalline precipitate of ammonium acid tartrate. The addition of a little sodium acetate, and rubbing the inside walls of the glass vessel with a stirring rod, will hasten the formation of the precipitate:

$$H_2C_4H_4O_6 + NH_4^+ \rightarrow \mathbf{NH_4HC_4H_4O_6} + H^+$$

The ammonium acid tartrate, like the corresponding potassium salt, is soluble in alkalies and mineral acids. It may be distinguished from the potassium salt by its behavior on ignition; carbon alone is left behind, and the residue does not effervesce with hydrochloric acid; furthermore, ammonium acid tartrate will give off ammonia on being heated with caustic soda solution.

8. **The Nessler test.** — The above-mentioned reactions are not suitable for the detection of the very small amounts of ammonia or of ammonium ions that are found in drinking water. In such cases Nessler's reagent is used (an alkaline solution of

* Riegler, *Chem.-Ztg.*, 21, Rep. 307.

potassium mercuric iodide). Large amounts of ammonia produce a brown precipitate,

$$2\ K_2HgI_4 + 4\ OH^- + NH_4^+ \rightarrow NHg_2I \cdot H_2O + 3\ H_2O + 4\ K^+ + 7\ I^-$$

The precipitate is the iodide of the so-called *Millon's base;* its structural formula is probably $O\langle^{Hg}_{Hg}\rangle NH_2 \cdot I$. The corresponding black nitrate is formed in the test for ammonia with mercurous nitrate paper. The iodide of Millon's base has such a remarkable coloring power that mere traces of the ammonium ion can be detected by the yellow or brown color imparted to the solution. The test is obtained with ordinary distilled water. Since ammonia is often present in water as a result of its contact with decaying organic matter, the test for ammonia helps to determine whether a water is suitable for drinking. The test is called the *Nessler test,* and the alkaline solution of potassium mercuric iodide is called *Nessler's reagent.*

Water free from ammonia should be used in preparing the Nessler reagent. Some sodium carbonate and a little potassium permanganate is added to ordinary distilled water, which is then redistilled, rejecting the first fourth and last sixth of the distillate; the middle portion is the so-called *best water* of the chemical laboratory. For the most accurate work, Nessler's reagent should be prepared with such water (cf. p. 91), and the test should be made in a laboratory from which ammonium fumes are absent.

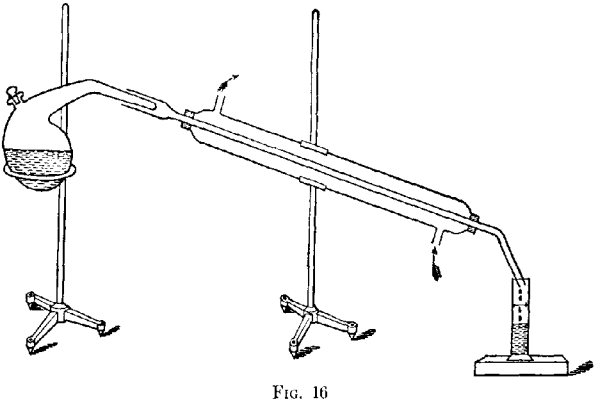


FIG. 16

To test a water for the presence of traces of ammonium ions, the apparatus shown in Fig. 16 may be used. First of all, the apparatus itself must be freed from all traces of ammonium salt. To accomplish this, place about 50 ml of water in the retort, add 1 ml of a boiled, saturated solution of sodium carbonate, and distil with the neck of the retort introduced well into the condenser tube. It is advisable not to use a rubber connection between the retort and the condenser; the condensed water serves to make a sufficiently tight connection.

Continue distilling until 50 ml of the distillate placed in a white glass graduate or in a so-called Nessler tube, and treated with 1 ml of Nessler reagent, will show no sign of color after standing five minutes. The apparatus is then ready for the test.

Empty the retort and refill it with 500 ml of the water to be tested, add 1 ml of the saturated sodium carbonate solution, distil, and collect the first 50 ml of distillate. If as much as 0.2 mg of ammonium is present, a distinct precipitate forms on adding 1 ml of Nessler's solution and stirring; a pronounced yellow color is obtained with much smaller quantities. If mere traces of ammonium are present, the yellow color appears only on standing. By comparing the depth of color with that similarly produced with known quantities of ammonium chloride, a very close estimate of the exact quantity of ammonium present can be made.

Reactions in the Dry Way

All ammonium salts are relatively unstable compounds, the degree of stability depending, in general, upon the strength of the acid which is combined with the ammonium. The carbonate decomposes appreciably at ordinary temperatures and when exposed to the air gradually disappears as ammonia, carbon dioxide, and water. Heating in a closed tube causes the decomposition of all ammonium salts, and either ammonia or some other volatile nitrogen compound escapes.

If the acid is volatile at the decomposition temperature, the whole salt is volatilized, often without first melting, and when the vapors of ammonia and acid are cooled the solid again forms. This explains the fumes of ammonium salt that result when ammonium salts are expelled from a solid residue obtained by evaporation of a solution, and it explains the sublimate formed when ammonium chloride is heated in a closed tube. The acids which form salts that are not volatilized are boric, phosphoric, chromic, molybdic, tungstic, and vanadic acids.

It must be remembered, however, that ammonia with its negative valence of three contains nitrogen in its lowest state of oxidation. When the decomposition of the original ammonium salt takes place, therefore, there is often an oxidation of the nitrogen. Thus the decomposition of the nitrate results in the formation of nitrous oxide, N_2O, and the decomposition of the nitrite, sulfate, and dichromate yields nitrogen gas.

The closed-tube reactions of typical ammonium compounds may be expressed by the following equations:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

$$NH_4NO_3 \rightarrow 2\,H_2O + N_2O$$

$$NH_4NO_2 \rightarrow 2\,H_2O + N_2$$

$$3\,(NH_4)_2SO_4 \rightarrow N_2 + 4\,NH_3 + 6\,H_2O + 3\,SO_2$$

$$(NH_4)_2C_2O_4 \rightarrow 2\,NH_3 + H_2O + CO + CO_2$$

ANALYSIS OF GROUP V

TABLE VII. — ANALYSIS OF GROUP V

<table>
<tr><td colspan="3">Filtrate from Group IV may contain NH_4^+, K^+ and Na^+. Evaporate and ignite the residue. Dissolve in water, add $BaCl_2$ (to remove SO_4^{--}) and then $(NH_4)_2CO_3$ (to remove Ba^{++}). Evaporate and ignite again. (1)</td></tr>
<tr><td>Vapor: NH_4 salts. Test the original substance for NH_4^+ by boiling with NaOH. (4)</td><td colspan="2">Residue: KCl, NaCl. Add $HClO_4$, evaporate, cool, and add alcohol. (2)</td></tr>
<tr><td></td><td>Residue: $KClO_4$. Dissolve in hot water, add $Na_3Co(NO_2)_6$ to precipitate yellow $K_2NaCo(NO_2)_6$. (2)</td><td>Solution: $NaClO_4$. Saturate with HCl gas. (3)</td></tr>
<tr><td></td><td></td><td>Precipitate: NaCl. Dissolve in water and add KH_2SbO_4 to precipitate white crystalline NaH_2SbO_4.</td><td>Filtrate: Reject.</td></tr>
</table>

PROCEDURE

1. *Removal of Ammonium Salts.* Evaporate the solution to dryness in a small casserole and ignite the residue, at first moderately and then at a temperature below redness, until no more white fumes are evolved. Keep the dish in motion over a small flame and heat the sides as well as the bottom. Cool; add 5 ml of water and 2–10 ml of $BaCl_2$ solution to remove sulfate. Even when no sulfate is present in the original substance, and when no sulfuric acid has been used in the analysis, a little sulfate may be formed from decomposition of the ammonium sulfide reagent used in precipitating the third group. Sulfate must be absent as otherwise Na_2SO_4 will precipitate on adding alcohol in the potassium test. Heat to boiling for two or three minutes and filter off the $BaSO_4$. To the filtrate add 5 ml of $(NH_4)_2CO_3$ reagent, let the mixture stand five minutes, heat nearly to boiling, and filter off the $BaCO_3$. Evaporate the solution to dryness just as described above. Cool the dish, add 5 ml of water, and filter through a small filter. Evaporate the filtrate to dryness once more and ignite again. A white residue, which may be difficult to see in the porcelain dish, indicates the presence of KCl or NaCl.

2. *Separation of Sodium and Potassium.* To the ignited residue, add 2–5 ml of 6-normal perchloric acid and evaporate, by keeping the dish in motion over a free flame, until thick fumes of perchloric acid are evolved. Cool, and when at room temperature add 10–20 ml of 95 per cent ethyl alcohol. Stir for several minutes, filter, and wash the pre-

cipitate with alcohol. Save the filtrate for the sodium test. Dissolve the potassium perchlorate precipitate in a few cubic centimeters of hot water, cool, and add 5 ml of sodium cobaltinitrite reagent. A yellow precipitate shows the presence of potassium.

3. Pour the alcoholic filtrate from the potassium perchlorate precipitate into a small flask and saturate it with dry HCl gas. Filter off the precipitated sodium chloride, wash it with a little alcohol, and reject the filtrate. (A dangerous explosion will result if this filtrate is heated or evaporated.) Dissolve the sodium chloride in 10 ml of water and evaporate the solution just to dryness. Add 1 ml of water and a few drops of potassium hydroxide solution to make the solution alkaline. Add 2 ml of potassium antimonate solution and allow the mixture to stand for some time. A white crystalline precipitate shows the presence of sodium. If a flocculent precipitate is formed, the heavier sodium precipitate can usually be discovered if the mixture is shaken and after a few seconds decanted off from the heavier sodium antimonate which usually adheres to the glass.

4. *Test for Ammonium.* Place a little of the original substance (corresponding to about 0.25 g of solid) in a test tube, add about 2 ml of 6 *N* sodium hydroxide, heat nearly to boiling, and hold a piece of red litmus paper, wrapped around the end of a stirring rod, in the escaping vapors. Take care not to allow any of the caustic alkali to come in contact with the litmus either by spattering or by allowing the paper to touch the sides of the test tube. Some idea of the quantity of ammonium present can be obtained from the odor. If it is desired to test for traces of ammonium, carry out the Nessler test as described on page 293.

Quiz Questions

1. (*a*) Explain the principle of the sepn. of Na from K by the $HClO_4$ method.
(*b*) Name 3 relatively insol. K salts and write formulas.
(*c*) Explain the confirmatory test for Na, write the formula of the final substance prepared and state its important physical properties.
2. (*a*) How would you detect NH_4 in an unknown? Where would you test for it?
(*b*) Explain one other test for NH_4^+. How should it be made?
3. What would happen if a soln. of $HClO_4$ and alc. were heated over a free flame?
4. Why is SO_4^{--} removed and why is it usually present?
5. If sodium cobaltinitrite soln. is 0.3 *N* in $Na_3Co(NO_2)_6$, 0.3 *N* in $NaNO_2$, and 1 *N* in HAcO, how many g of each substance is contained in 1 ml of the reagent?
6. Give a tabular outline of the method for analyzing the alkali group.
7. How is KH_2SbO_4 soln. made?
8. Write an equation for the oxidation of alc. to water and CO_2 by the action of $HClO_4$, itself reduced to HCl. Calc. the vol. of HCl and of CO_2 formed if measured dry at 80° and 780 mm pressure.
9. What wt. of $K_2NaCo(NO_2)_6$ can be formed from 0.25 g of KCl?
10. If a ppt. of $K_2NaCo(NO_2)_6$ is treated with $KMnO_4$ in the presence of acid, the products formed are K^+, Na^+, Mn^{++}, Co^{++}, NO_3^- and H_2O. Write an equation for the reaction.

PART III. REACTIONS OF THE ACID CONSTITUENTS OR ANIONS

DIVISION OF THE ACIDS INTO GROUPS

The classification of the acids which is given here was first published by R. Bunsen in 1878 (in manuscript form) for the use of his students; it was adopted (with his consent) by V. Meyer and F. P. Treadwell in their "Tabellen zur qualitativen Analyse." It is based upon the different solubilities of the barium and silver salts.

Group I

Acids whose silver salts are insoluble in water and in nitric acid, but whose barium salts are soluble in water.

To this group belong hydrochloric, hydrobromic, hydriodic, hydrocyanic, ferrocyanic, ferricyanic, cobalticyanic, thiocyanic, and hypochlorous acids.

Group II

Acids whose silver salts are soluble in nitric acid, but are insoluble, or difficultly soluble, in water, and whose barium salts are soluble in water.

To this group belong hydrosulfuric (hydrogen sulfide), hydroselenic, hydrotelluric, nitrous, acetic, cyanic, hypophosphorous, and hydrazoic acids.

Group III

Acids whose silver salts are white and soluble in nitric acid, but whose barium salts are difficultly soluble or insoluble in water, but soluble in nitric acid.

To this group belong sulfurous, selenous, tellurous, phosphorous, carbonic, oxalic, iodic, boric, molybdic, selenic and telluric, tartaric, citric, and meta- and pyrophosphoric acids.

Group IV

Acids whose silver salts are colored and soluble in nitric acid, but whose barium salts are insoluble in water and soluble in nitric acid.

To this group belong phosphoric, arsenic, arsenious, vanadic, thiosulfuric, chromic, and periodic acids.

Group V

Acids whose silver and barium salts are soluble in water.

To this group belong nitric, chloric, perchloric, persulfuric, and the manganic acids.

Group VI

Acids whose silver salts are soluble in water, but whose barium salts are insoluble in nitric acid.

To this group belong sulfuric, hydrofluoric, and fluosilicic acids.

Group VII

Non-volatile acids, which form soluble salts only with the alkalies.

To this group belong silicic, tungstic, titanic, columbic, and tantalic acids.

GROUP I

Silver Nitrate produces a precipitate insoluble in nitric acid.
Barium Chloride causes no precipitation.

HYDROCHLORIC ACID, HCl

Occurrence. — Hydrochloric acid is found free in nature, but in small quantities (for example, in the exhalations of active volcanoes); its salts, however, are exceedingly common, especially those with the alkalies. (See these.)

The term hydrochloric acid, as ordinarily used in analytical chemistry, refers to an approximately 12 *N* aqueous solution of density 1.2 containing about 39.1 per cent of hydrogen chloride by weight. In the old, dualistic nomenclature an acid was supposed to be the oxide of a negative element and water, and oxygen was regarded as an essential constituent of all acids. For this reason, hydrogen chloride itself was not regarded as an acid. Today the presence of replaceable hydrogen, or the formation of hydrogen ions in aqueous solution, is held to be the essential characteristic of an acid, and some chemists still hold that hydrogen chloride is not an acid until it is dissolved in water and forms hydrogen ions. Most chemists, however, regard hydrogen chloride, HCl, as hydrochloric acid. The anhydrous acid is a gas at ordinary temperatures. When solidified it melts at $-111°$ and boils at $-85°$; the critical temperature is 51.3°, and the critical pressure, 83 atmospheres. It is a colorless gas with a penetrating, suffocating, and irritating odor. Acid of density 1.10 containing 20.4 per cent of HCl has a constant boiling point at 110°. From this constant boiling point, one might conclude that it was a pure compound, but it is merely a solution of the gas in water and corresponds approximately to a 6-normal solution. Acid of density greater than 1.10 gives off hydrogen chloride gas faster than water, but if the density is less than 1.10 water evaporates faster than the hydrogen chloride; in both cases the mixture tends to approach the constant-boiling acid by evaporation or by boiling.

Preparation. — Hydrochloric acid is usually made by the action of sulfuric acid upon common salt. When sulfuric acid is allowed to act upon sodium chloride, a considerable evolution of hydrochloric acid takes place even in the cold, with the formation of sodium bisulfate:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$$

On heating, the sodium bisulfate reacts with more sodium chloride:

$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl\uparrow$$

When only one hydrogen of a dibasic acid is replaced by metal, the resulting salt is usually designated by placing the prefix *bi* before the name of the anion: sodium bicarbonate, $NaHCO_3$; sodium bisulfate, $NaHSO_4$, etc. There is *twice* as much acid per equivalent of base as in the normal salt.

Hydrochloric acid gas may be prepared conveniently in the laboratory by dropping concentrated sulfuric acid into 12-normal hydrochloric acid. It is also formed by the action of water on many acid chlorides:

$$PCl_3 + 3\ H_2O \rightarrow H_3PO_3 + 3\ HCl$$

Properties. — Hydrochloric acid is readily soluble in water (one volume of water dissolves, at 18° C, 451 volumes of hydrochloric acid). The specific gravity of the saturated, aqueous solution is 1.21, and 100 ml of this solution contains 50.7 g of anhydrous hydrogen chloride. The concentrated hydrochloric acid of the laboratory is about 12-normal, and contains 36 to 39 per cent of the gas by weight. The aqueous solution of hydrochloric acid is one of our strongest acids. In dilute solution it is almost entirely ionized,

$$HCl \rightleftarrows H^+ + Cl^-$$

and such a solution is a good conductor of electricity.

The behavior of hydrochloric acid on oxidation is characteristic; water is formed and chlorine is set free:

$$4\ HCl + O_2 \rightleftarrows 2\ H_2O + 2\ Cl_2\uparrow$$

This oxidation will not take place on exposure to atmospheric, or even pure, oxygen, but only by treatment with strong oxidizing agents such as: *The peroxides of the heavy metals, all nitrates, nitrites, chlorates, hypochlorites, chromates, selenates,* and *tellurates.*

The peroxides of the light metals do not yield chlorine, but hydrogen peroxide:

$$BaO_2 + 2\ HCl \rightarrow BaCl_2 + H_2O_2$$

1. Oxidation of Hydrochloric Acid by Means of Peroxides

(*a*) *By manganese dioxide:*

$$4\ HCl + \mathbf{MnO_2} \rightarrow 2\ H_2O + MnCl_2 + Cl_2\uparrow$$

The manganese is reduced from the quadrivalent to the bivalent condition and the negatively charged chlorine atom becomes neutral chlorine gas. Thus one atom of manganese oxidizes two atoms of chlorine.

Some other acid, preferably sulfuric, can be used to combine with the manganese and then the yield of chlorine from a given quantity of hydrochloric acid will be twice as large:

$$\mathbf{MnO_2} + 2\ HCl + H_2SO_4 \rightarrow MnSO_4 + 2\ H_2O + Cl_2\uparrow$$

(*b*) *By lead peroxide:*

$$4\ HCl + PbO_2 \rightarrow 2\ H_2O + PbCl_2 + Cl_2\uparrow$$

(*c*) *By chromium trioxide (chromic acid anhydride):*

$$2\ CrO_3 + 12\ HCl \rightarrow 6\ H_2O + 2\ CrCl_3 + 3\ Cl_2$$

2. Oxidation of Hydrochloric Acid by Nitric Acid, etc.

When concentrated nitric acid acts upon concentrated hydrochloric acid, the products of the reaction are water, nitrosyl chloride, and free chlorine:

$$HNO_3 + 3\ HCl \rightarrow 2\ H_2O + NOCl\uparrow + Cl_2\uparrow$$

In this reaction the valence of the nitrogen has been reduced from five to three, and two atoms of chlorine have been oxidized to form an electrically neutral chlorine molecule.

A mixture of one molecule of nitric acid with three of hydrochloric acid is known as *aqua regia*. The acids are usually mixed, not according to their weights, but according to their volumes.

Aqua regia, therefore, behaves very much like chlorine water but is more efficient because more chlorine can be formed in a small volume of solution and NOCl is also a good oxidizing agent. Nitrous, chloric, hypochlorous, selenic, and telluric acids all react similarly with hydrochloric acid.

Hydrochloric acid is *monobasic;* its salts are called *chlorides*.

Solubility of Chlorides

Nearly all chlorides are soluble in water, but the following are difficultly soluble: mercurous chloride, Hg_2Cl_2; silver chloride, AgCl; cuprous chloride, Cu_2Cl_2; lead chloride, $PbCl_2$; thallous chloride, TlCl; aurous chloride, AuCl; platinous chloride, $PtCl_2$; bismuth oxychloride, BiOCl; antimony oxychloride, SbOCl; mercuric oxychloride, Hg_2Cl_2O.

All these chlorides which are insoluble in water are more soluble in strong hydrochloric acid. Aurous chloride and platinous chloride dissolve readily in aqua regia, as a result of being oxidized, but silver chloride is not very soluble even in aqua regia. Lead chloride is soluble in hot water.

By boiling the insoluble chlorides with a concentrated solution of sodium carbonate, all, with the exception of silver chloride, are readily decomposed, *e.g.:*

$$Hg_2Cl_2 + Na_2CO_3 \rightarrow 2\ NaCl + CO_2 \uparrow + Hg_2O$$

By filtration, a chloride solution is obtained which is free from heavy metal.

By fusing with sodium carbonate, even silver chloride is decomposed,

$$4\ AgCl + 2\ Na_2CO_3 \rightarrow 4\ NaCl + 2\ CO_2 \uparrow + O_2 \uparrow + 4\ Ag$$

and silver chloride may also be decomposed by treatment with metals and dilute acid (cf. p. 104).

The deliquescent chlorides (lithium, calcium, and strontium) are all soluble in absolute alcohol and in amyl alcohol.

The chlorides of sodium and barium are quite insoluble in concentrated hydrochloric acid; they can, therefore, be easily separated from other chlorides which are soluble in water by saturating the solution with hydrochloric acid gas.

Almost all chlorides are insoluble in ether, with the exception of mercuric, stannous, stannic, auric, and ferric chlorides.

Reactions in the Wet Way

A neutral solution of an alkali chloride should be used for these reactions. All chlorides except those of mercury and cadmium are quite completely ionized in aqueous solution, so that it is a matter of indifference which chloride is taken for the following reactions, provided no independent reaction takes place because of the presence of the cation.

1. **Dilute Sulfuric Acid** (1 : 10) produces no reaction, even on warming.

2. **Concentrated Sulfuric Acid** decomposes a solid chloride almost completely in the cold, completely on warming. Sulfate and colorless hydrochloric acid gas result from this reaction; the latter is easily

recognized by its odor, by the clouds which it forms in moist air or with ammonia vapors (obtained by holding a glass rod wet with ammonia near the test tube), and by its turning moist, blue litmus paper red. Water is not made turbid by hydrochloric acid (difference from fluosilicic acid).

Silver chloride and mercurous chloride are decomposed with difficulty by sulfuric acid, the latter with evolution of sulfur dioxide; the *mercurous* sulfate (which is at first formed) is oxidized (at the expense of the oxygen of the sulfuric acid) to *mercuric* sulfate:

$$Hg_2Cl_2 + H_2SO_4 \rightarrow Hg_2SO_4 + 2\,HCl$$

$$Hg_2SO_4 + 2\,H_2SO_4 \rightarrow 2\,HgSO_4 + 2\,H_2O + SO_2\uparrow$$

If a chloride and an oxidizing agent are heated with concentrated sulfuric acid, free chlorine is evolved (cf. p. 300).

3. **Phosphoric Acid**, heated with a chloride, similarly causes the evolution of hydrochloric acid gas. If an oxidizing agent is present at the same time, chlorine gas is evolved.

4. **Silver Nitrate** produces a white, curdy precipitate of silver chloride,

$$Cl^- + Ag^+ \rightarrow \mathbf{AgCl}$$

insoluble in nitric acid, soluble in ammonia, potassium cyanide, and sodium thiosulfate solutions. (See Silver.)

From a solution of silver chloride in ammonia, acids reprecipitate silver chloride. From a solution in potassium cyanide, acids precipitate silver cyanide. If it is desired to test a solution of ferrous sulfate for the presence of a small amount of chloride, it must be strongly acidified with nitric acid, as otherwise a precipitate of metallic silver will be obtained, which may cause confusion (cf. p. 102). The best way to test the solution of ferrous sulfate for hydrochloric acid is to add sodium carbonate solution until alkaline, boil, and filter. In the filtrate the acids originally present are now in the form of their sodium salts, in the presence of an excess of sodium carbonate; the solution should be made acid with nitric acid before the silver nitrate is added.

The detection of chlorine when present in the form of chloride of a heavy metal is accomplished in a similar manner; and, with the exception of silver chloride, any insoluble chloride may be decomposed in the same way, by boiling with sodium carbonate solution.

In order to detect the presence of chlorine in silver chloride, treat it with dilute sulfuric acid and zinc (p. 104), after a short time pour off the solution from the deposited silver and test it with silver nitrate. Or, fuse the silver chloride with sodium carbonate, extract the melt with water, filter, acidify with nitric acid, and test with silver nitrate.

5. **Mercurous Nitrate** and **Lead Acetate** give precipitates of mercurous chloride and lead chloride. From auric chloride solution, lead acetate precipitates a double chloride of lead and gold.

6. **Potassium Dichromate and Sulfuric Acid.** — If a dry chloride is mixed with potassium dichromate and covered with concentrated sulfuric acid, and the mixture is heated in a small retort, brownish vapors are given off which condense, in the receiver, to a brown liquid (chromyl chloride, CrO_2Cl_2):

$$K_2Cr_2O_7 + 4\,NaCl + 6\,H_2SO_4 \rightarrow 3\,H_2O + 4\,NaHSO_4 + 2\,KHSO_4 + 2\,CrO_2Cl_2$$

Chromyl chloride is an acid chloride, and is, therefore, decomposed by water into chromic and hydrochloric acids:

$$CrO_2Cl_2 + 2\,H_2O \rightarrow H_2CrO_4 + 2\,HCl$$

On adding alkali hydroxide to the distillate, an alkali chloride and a yellow alkali chromate are obtained. If the solution is then acidified, some ether and a little hydrogen peroxide added, and the liquid shaken, the upper ether layer will be colored blue, showing the presence of chromium; and the presence of chromium indicates that a chloride was originally present (difference from bromide and iodide).

The test can be made to detect as little as 1.5 γ of chlorine by taking the solid substance, or the residue obtained by evaporating a solution to dryness, and adding a little powdered potassium dichromate and a very little concentrated sulfuric acid. Then on distilling in a very small apparatus and passing the vapors into a 1 per cent solution of diphenylcarbazide (cf. p. 121) the chromyl chloride will cause the color of the diphenylcarbazide to become violet.

7. **Potassium Permanganate** oxidizes a chloride in acid solution. On the other hand, hydrobromic and hydriodic acids are oxidized much more readily than hydrochloric acid.

Behavior of Chlorides on Ignition

The chlorides of the alkalies and alkaline earths melt (without perceptible decomposition) on being heated in the air. The chlorides of the sesquioxides are decomposed, more or less completely, on being ignited in the air. Thus, ferric chloride is almost quantitatively decomposed into ferric oxide, with loss of chlorine:

$$4\,FeCl_3 + 3\,O_2 \rightarrow 2\,Fe_2O_3 + 6\,Cl_2\uparrow$$

In the presence of hydrochloric acid, or ammonium chloride, ferric chloride may be volatilized completely without any decomposition.

The chlorides of gold and of the platinum metals are readily decomposed into chlorine and metal:

$$2\,AuCl_3 \rightarrow 2\,Au + 3\,Cl_2\uparrow$$
$$PtCl_4 \rightarrow Pt + 2\,Cl_2\uparrow$$

The remaining chlorides are mostly volatile, without perceptible decomposition except in the case of ammonium chloride (cf. p. 294).

DETECTION OF CHLORINE IN NON-ELECTROLYTES

Besides uniting with metals and with hydrogen, chlorine also forms compounds with the metalloids; *e.g.*, PCl_3, PCl_5, $AsCl_3$, $AsCl_5$, $SbCl_3$, $SbCl_5$, CCl_4, $SiCl_4$, etc.

All these compounds, which may be regarded as acid chlorides, are decomposed by water with the formation of hydrochloric acid, which can be tested for in the usual way. The hydrolysis usually takes place at the ordinary temperatures. Thus, phosphorus trichloride yields with water phosphorous acid and hydrochloric acid,

$$PCl_3 + 3\ HOH \rightarrow H_3PO_3 + 3\ HCl$$

and phosphorus pentachloride yields phosphoric acid and hydrochloric acid:

$$PCl_5 + 4\ HOH \rightarrow H_3PO_4 + 5\ HCl$$

The remaining acid chlorides are decomposed in a similar way by water at the ordinary temperature, with the exception of carbon tetrachloride, which is decomposed by water only by heating in a closed tube:

$$CCl_4 + 2\ H_2O \rightarrow CO_2 + 4\ HCl$$

Chlorine acts upon a great many hydrocarbons, forming substitution products which are non-electrolytes, and consequently will not give the chloride tests; for example, if chloroform, $CHCl_3$, is shaken with a solution of aqueous silver nitrate, it will not yield a precipitate of silver chloride. In order to test such compounds for chlorine (as is frequently necessary in the study of organic compounds), the chlorine must be changed to hydrochloric acid by one of the following methods:

1. **Carius' Method.** — By heating the compound in a sealed glass tube with concentrated nitric acid, in the presence of silver nitrate, the compound is completely decomposed; all the chlorine is changed to silver chloride, which can be filtered off, and, after treatment with zinc and dilute sulfuric acid, can be tested as above. The precautions to be taken in sealing and opening the tube are described in Vol. II.

2. **By Heating with Lime.** — Place a layer of granular lime (free from chloride) then a mixture of the substance to be tested and lime, and finally another layer of lime in a small glass tube, which should be about 25 cm long and about 1 cm wide. By gently tapping the tube, open up a canal between the upper wall of the tube and the substance, through which the gases evolved may escape. Place the tube horizontally in a small combustion furnace and heat (first the front layer of lime, then the back layer, and finally the entire contents of the tube) to a dull red heat. By this means the organic substance will be completely decomposed, and the chlorine will be found combined with the lime in the form of calcium chloride. Cool, dissolve the contents of the tube in dilute nitric acid, filter off the carbon, and test the filtrate with silver nitrate for chloride ions.

3. **Treatment with Sodium.** — Place a small amount of the dry substance to be tested in a small test tube, add a small piece of sodium (freed from petroleum), and cover the metal with another layer of the substance. Heat the tube in the gas flame; the decomposition takes place suddenly with incandescence. Place the hot tube and its contents in a small beaker containing water (which breaks the tube); sodium chloride dissolves with other sodium compounds. Filter the solution, make acid with nitric acid, and test with silver nitrate for halogens.

Free Chlorine

Chlorine, whether produced by the oxidation of hydrochloric acid or by igniting certain chlorides, is a greenish yellow gas with a suffocating odor. It is absorbed by water (1 volume of water absorbs at 10° C about 2.7 volumes of chlorine gas), forming chlorine water, a yellowish green liquid, and a poor conductor of electricity (although better than pure water, showing that some ions are present). Chlorine decomposes water to a slight extent, forming hydrochloric acid and hypochlorous acid:

$$H_2O + Cl_2 \rightleftarrows 2\ H^+ + Cl^- + ClO^-$$

In this reaction one atom of chlorine is oxidized to a positive valence of one and another atom of chlorine is reduced to a negative valence of one (cf. p. 228). This reaction, as the application of the mass-action law indicates, is favored by the presence of hydroxide ions and hindered by the presence of hydrogen ions. If, besides water, which is only slightly ionized, dilute alkali is present, the reaction takes place quantitatively from left to right:

$$Cl_2 + 2\ OH^- \rightarrow Cl^- + ClO^- + H_2O$$

The decomposition of chlorine water takes place slowly in the dark, but more rapidly in the light, and in the presence of oxidizable substances. The bleaching action of chlorine water depends upon its oxidizing power.

Chlorine water is a strong oxidizing agent.

If a solution of potassium iodide is treated with chlorine water, iodine is set free, and the solution turns yellow to brown:

$$2\ KI + Cl_2 \rightarrow 2\ KCl + I_2$$

If the yellow solution is shaken with carbon disulfide, or chloroform, a more highly colored, violet, non-aqueous solution of iodine is obtained (cf. p. 14). By the addition of more chlorine water the solution becomes colorless, owing to the oxidation of the iodine to colorless iodic acid:

$$I_2 + 6\ H_2O + 5\ Cl_2 \rightarrow 10\ HCl + 2\ HIO_3$$

The free iodine can also be detected by the addition of some starch paste (instead of carbon disulfide, etc.), which is turned blue by iodine.

1. **Silver Nitrate** gives a white precipitate of silver chloride when added to chlorine water; this precipitation, however, is not quantitative, for one-sixth of the chlorine is changed into soluble silver chlorate:

$$3\ Cl_2 + 5\ Ag^+ + 3\ H_2O \rightarrow 5\ AgCl + ClO_3^- + 6\ H^+$$

On adding a slight excess of sulfurous acid to chlorine water, the chlorine is readily and completely changed into hydrochloric acid:

$$Cl_2 + H_2O + H_2SO_3 \rightarrow H_2SO_4 + 2\ HCl$$

From this solution the chlorine can be precipitated quantitatively by silver ions.

Chlorine may also be easily changed into the form of a chloride by the action of ammonia (cf. p. 222):

$$3\ Cl_2 + 8\ NH_3 \rightarrow 6\ NH_4Cl + N_2\uparrow$$

Chlorine can be changed to a chloride by the action of hydrogen peroxide in the presence of sodium or potassium hydroxide:

$$Cl_2 + 2\ OH^- + H_2O_2 \rightarrow 2\ H_2O + 2\ Cl^- + O_2\uparrow$$

2. **Metallic Mercury** is attacked by chlorine at ordinary temperatures, forming insoluble mercurous chloride:

$$Hg_2 + Cl_2 \rightarrow Hg_2Cl_2$$

If therefore chlorine water is shaken with metallic mercury until it no longer smells of chlorine, a neutral solution is obtained which contains no free chlorine. If hydrochloric acid was originally present, the solution now reacts acid and gives a precipitate with silver nitrate, for metallic mercury is not attacked by hydrochloric acid. This reaction is used as a test for hydrochloric acid in the presence of chlorine.

3. **Metallic Zinc** also reacts with chlorine water,

$$Zn + Cl_2 \rightarrow Zn^{++} + 2\ Cl^-$$

4. **Indigo Solution** is decolorized by chlorine water. If a dilute solution of indigo is used, the discharge of the color is a sensitive test for chlorine.

5. **Iodo-starch Paper** (paper which has been dipped in starch paste containing potassium iodide) is turned blue by chlorine. The test is also delicate when starch paste containing zinc iodide in solution is used.

HYPOCHLOROUS ACID, HOCl

Hypochlorous acid in the free state is unknown. Its anhydride, Cl_2O, is a deep yellow gas at ordinary temperatures and has an unpleasant, irritating odor. It explodes into chlorine and oxygen on being heated. Dilute aqueous solutions of hypochlorous acid can be distilled. The acid is very weak and has the ionization constant of 3.7×10^{-8} at 17°.

Preparation. — A solution of free hypochlorous acid is obtained by shaking chlorine water with yellow mercuric oxide until the solution no longer smells of chlorine:

$$2\ HgO + 2\ Cl_2 + H_2O \rightarrow (HgCl)_2O + 2\ HOCl$$

Brown, insoluble mercuric basic chloride is formed by the reaction, and the solution contains hypochlorous acid. If the solution is poured off from the insoluble basic mercuric salt and distilled, a pure solution of hypochlorous acid will be obtained, which, however, cannot be kept long in the light, for it decomposes into hydrochloric acid and oxygen:

$$2\ HOCl \rightarrow 2\ HCl + O_2\uparrow$$

Properties. — Hypochlorous acid is a vigorous bleaching agent; litmus and indigo are quickly decolorized.

The alkali salts of hypochlorous acid (hypochlorites) are obtained by neutralizing the acid with dilute sodium or potassium hydroxide, or, more conveniently, by the action of chlorine on a dilute caustic alkali solution:

$$Cl_2 + 2\ OH^- \rightarrow Cl^- + ClO^- + H_2O$$

The ammonium salt cannot be prepared except at very low temperatures, because the nitrogen of ammonia is so readily oxidized (cf. p. 222).

All hypochlorites are readily changed, on warming, into chlorate* and chloride (cf. p. 228):

$$3\ KClO \rightarrow 2\ KCl + KClO_3$$

Consequently hypochlorites must always be prepared in cold, dilute solution.

The most important commercial hypochlorite is the so-called "chloride of lime," which is obtained by passing chlorine gas over lime at the ordinary temperature. The product formed can be regarded as a mixture of calcium chloride, calcium hypochlorite, and calcium oxide with a little water. A dilute solution of sodium hypochlorite is sold under the names "chlorox," "oxol," "zonite," etc. Javelle water is a dilute aqueous solution of KClO and KCl, and Dakin's Carrel solution is a 0.45 per cent aqueous solution of NaClO.

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* In the presence of 40 per cent or more of caustic potash, potassium hypochlorite on being heated decomposes into chloride with evolution of oxygen and the formation of no chlorate (F. Winteler, *Z. angew. Chem.*, **33**, p. 778 (1902).)

Reactions in the Wet Way

All hypochlorites are soluble in water, and are decomposed by acids (even carbonic acid).

1. **Hydrochloric Acid** is oxidized by hypochlorites with evolution of chlorine:

$$ClO^- + Cl^- + 2\,H^+ \rightarrow H_2O + Cl_2\uparrow$$

The reaction is favored by the presence of hydrogen ions. The reverse reaction is favored by the presence of hydroxide ions (cf. p. 305).

2. **Sulfuric Acid** decomposes hypochlorites, setting free hypochlorous acid:

$$NaOCl + H_2SO_4 \rightarrow NaHSO_4 + HOCl$$

and carbonic acid acts similarly though less energetically:

$$2\,NaOCl + H_2CO_3 \rightarrow Na_2CO_3 + 2\,HOCl$$

It is due to the fact that hypochlorites are so readily decomposed with the formation of chlorine that they act as strong bleaching agents; indigo solution (a solution of indigo in sulfuric acid) is immediately decolorized.

Hypochlorites act as oxidizing agents not only in acid solutions, but also in alkaline solutions at ordinary temperatures (difference from chlorates), many metallic hydroxides being oxidized by them to higher hydroxides. Thus, ferrous hydroxide is readily oxidized to reddish brown ferric hydroxide:

$$2\,Fe(OH)_2 + ClO^- + H_2O \rightarrow Cl^- + 2\,Fe(OH)_3$$

and similarly lead, manganous, nickelous, and cobaltous hydroxides are oxidized to brownish black hydroxides.

Less than 1 mg of hypochlorite can be detected by boiling with lead acetate solution:

$$Pb^{++} + ClO^- + H_2O \rightarrow PbO_2 + 2\,H^+ + Cl^-$$

If a peroxide is likely to be present, the solution must first be acidified with acetic acid before applying the test (cf. p. 288).

3. **Silver Nitrate** causes in solutions of hypochlorites an incomplete precipitation of silver chloride. One-third of the chlorine remains in solution in the form of chlorate:

$$3\,ClO^- + 2\,Ag^+ \rightarrow ClO_3^- + 2\,AgCl$$

Hypochlorous acid is distinguished from chlorine by its behavior toward mercury; from hydrochloric acid by its oxidizing action; and from chloric acid by its being partly precipitated by silver nitrate, and by its oxidizing action in alkaline solutions.

4. **Iodo-Starch Paper** is turned blue by hypochlorites in weakly alkaline solutions, owing to the separation of iodine:

$$2\,KI + NaOCl + H_2O \rightarrow 2\,KOH + NaCl + I_2$$

$$2\,I^- + ClO^- + H_2O \rightleftarrows Cl^- + 2\,OH^- + I_2$$

The extent to which the reaction takes place depends upon the concentration of the hydroxide ion; only in dilute alkali will enough iodine be formed to produce the blue coloration with the starch.

5. **Manganous Chloride** in concentrated hydrochloric acid is darkened by hypochlorous acid. This test merely shows that an oxidizer is present.

6. **Metallic Mercury.** — If a solution containing free hypochlorous acid is shaken with metallic mercury, brown basic mercuric chloride is formed, insoluble in water, but soluble in hydrochloric acid:

$$2\,Hg + 2\,HOCl \rightarrow (HgCl)_2O + H_2O$$

Under these same conditions free chlorine forms, on being shaken with mercury, white mercurous chloride, which is insoluble in hydrochloric acid.

This property is utilized in detecting hypochlorous acid in the presence of free chlorine. The mixture is shaken with mercury until a little of the solution no longer turns iodo-starch paper blue; the liquid is then carefully poured off, hydrochloric acid is added to the residue, and the mixture is shaken, when the basic chloride produced by hypochlorous acid goes into solution:

$$(HgCl)_2O + 2\,HCl \rightarrow H_2O + 2\,HgCl_2$$

while mercurous chloride remains undissolved.

If hydrogen sulfide is passed into the filtered solution, the formation of mercuric sulfide shows that hypochlorous acid was originally present.

The *salts* of hypochlorous acid behave differently toward mercury: they form insoluble mercuric oxide and a soluble chloride:

$$Hg + NaOCl \rightarrow HgO + NaCl$$

7. **Permanganate** solution is not decolorized by hypochlorous acid. **Litmus** and **indigo** are decomposed slowly in alkaline solution and more rapidly decolorized in the presence of acid. If a solution of arsenious acid is colored blue by indigo, the latter is not bleached until all the arsenious acid has been oxidized to arsenic acid.

HYDROBROMIC ACID, HBr

Occurrence.—Bromine compounds are always found in nature together with chlorine compounds; thus salts of hydrobromic acid are found in the ocean and in many mineral waters.

Preparation. — Hydrogen bromide can be prepared directly from hydrogen and bromine with the aid of a suitable catalyst, *e.g.*, platinum. It can be obtained by the action of a reducing agent, such as hydrogen sulfide or sulfur dioxide, upon bromine

$$Br_2 + SO_2 + 2\,H_2O \rightarrow H_2SO_4 + 2\,HBr$$

or by the hydrolysis of phosphorus tribromide

$$PBr_3 + 3\,HOH \rightarrow H_3PO_3 + 3\,HBr$$

Fairly pure hydrobromic acid can be obtained by adding sulfuric or phosphoric acid to an aqueous solution of an alkali bromide and distilling. If sulfuric acid is used, bromine is also formed as soon as the hot acid is about 9 *N* in concentration.

$$2\,NaBr + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HBr$$
$$2\,HBr + H_2SO_4 \rightarrow 2\,H_2O + SO_2 + Br_2$$

Properties. — Hydrogen bromide, HBr, like hydrogen chloride is a colorless gas with a suffocating odor which fumes in moist air and forms clouds of ammonium bromide on coming in contact with ammonia vapors. The critical temperature is 89.8° and the critical pressure about 84 atmospheres. Solid hydrogen bromide melts at −87°, and the liquid boils at −66.7°. The gas is very soluble in water; 100 g of water absorb 193 g of hydrogen bromide at room temperature. The solution with 47 per cent HBr, which corresponds closely to $HBr \cdot 5\,H_2O$, has a constant boiling point at 126°. When the term "hydrobromic acid" is used in chemical literature, it usually refers to an aqueous solution of the gas. Hydrobromic acid is less stable than hydrochloric acid and more stable than hydriodic acid.

Although hydrochloric acid can be kept in aqueous solution for an indefinitely long time, a solution of hydrobromic acid soon turns brown, owing to the separation of bromine. Hydrobromic acid is oxidized by atmospheric oxygen:

$$4\,HBr + O_2 \rightarrow 2\,H_2O + 2\,Br_2\uparrow$$

Owing to the slight solubility of cuprous bromide, and aided by the presence of a little free bromine, hydrobromic acid will dissolve copper, although this element is below hydrogen in the electromotive series (cf. pp. 43 and 129).

Hydrobromic acid is readily oxidized with separation of bromine, by peroxides, nitrates, chromates, etc., provided a concentrated solution of hydrobromic acid is used.

Hydrobromic acid is a monobasic acid; its salts are called bromides. It is one of the strongest acids, and the aqueous solutions are ionized to the same extent as solutions of hydrochloric acid.

The solubility of a bromide is similar to that of the corresponding chloride.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** (1 : 10) evolves no hydrobromic acid from bromides in the cold, but, on warming, does so from bromides of the alkalies.

2. **Concentrated Sulfuric Acid** causes evolution of hydrobromic acid and bromine from all bromides:

$$H_2SO_4 + 2\,Br^- \rightarrow SO_4^{--} + 2\,HBr$$

and

$$H_2SO_4 + 2\,HBr \rightarrow 2\,H_2O + SO_2\uparrow + Br_2\uparrow$$

The solution is brown, and, on warming, yellowish brown vapors are given off (difference from hydrochloric acid), which, since they contain hydrobromic acid, fume in moist air, have a suffocating odor, and do not render water turbid (difference from fluosilicic acid).

3. **Phosphoric Acid** causes the evolution of hydrobromic acid. If an oxidizing agent is also present, bromine is evolved.

4. **Silver Nitrate** produces a curdy, cream-colored precipitate of silver bromide, insoluble in nitric acid, but soluble in ammonia, potassium cyanide, and sodium thiosulfate. Silver bromide is less soluble than silver chloride.

Silver chloride, therefore, if digested with potassium bromide, will be changed into silver bromide.

$$AgCl + KBr \rightarrow AgBr + KCl$$

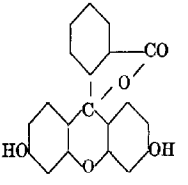
If, however, silver bromide is heated and treated with chlorine gas, it is readily changed into silver chloride:

$$2\,AgBr + Cl_2 \rightarrow 2\,AgCl + Br_2\uparrow$$

5. **Chlorine Water,** on being added to solutions of soluble bromides, sets free bromine, which is soluble in carbon disulfide or chloroform, forming a brown solution; but it is changed, by an excess of chlorine water, into yellowish chloride of bromine (BrCl) (difference from iodine).

6. **Fluorescein** is turned red by bromine liberated by the action of an oxidizing agent upon a bromide in the presence of acid.

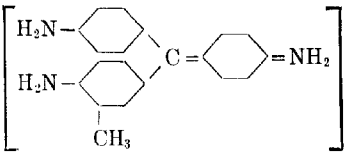
The yellow dyestuff, fluorescein, $C_{20}H_{12}O_5$ or



is changed to red tetrabromofluorescein (eosin) by the action of bromine. Bromine is liberated from bromide by the action of lead dioxide in the presence of acetic acid.

$$2\,Br^- + PbO_2 + 4\,HC_2H_3O_2 \rightarrow Pb(C_2H_3O_2)_2 + 2\,C_2H_3O_2^- + 2\,H_2O + Br_2$$

In a tiny flask place a drop of the solution to be tested, a few grains of solid lead dioxide, and some acetic acid. Instead of the lead dioxide and acetic acid a drop of 25 per cent chromic acid solution can be used. Heat and cause the vapors to come in contact with filter paper which has been impregnated with a saturated solution of fluorescein in 50 per cent alcohol. The test can be obtained with 2 γ of bromine.

7. The dyestuff **fuchsin,**  , forms a colorless addition product with bisulfite. If a solution of fuchsin which has been decolorized by adding sodium bisulfite, $NaHSO_3$, is acted upon by a little bromine, a blue bromine substitution product of the dyestuff is obtained. Since chlorine and iodine do not give this color test, it is useful for detecting small quantities of bromide in the presence of considerable iodide or chloride.

Place a drop of the solution to be tested, or a little of the solid substance, in a small tube and add 2–4 drops of a 25 per cent solution of chromic acid anhydride, CrO_3. Draw out the end of the tube to a capillary and in the capillary insert a drop of 0.1 per cent fuchsin solution which has been decolorized by adding a little sodium bisulfite, $NaHSO_3$. Heat carefully but do not boil. If a bromide is present a violet coloration will be obtained with as little as 3.2 γ of bromine.

8. **Nitrous Acid** does not cause the separation of bromine from a dilute bromide solution in the cold (difference from iodine).

9. **Potassium Dichromate,** in the presence of dilute sulfuric acid, does not cause separation of bromine from aqueous solutions of bromides; on shaking the solution with carbon disulfide, the latter remains colorless (difference from iodine).

10. **Potassium Dichromate** and **Concentrated Sulfuric Acid.** — On mixing a solid bromide with solid potassium dichromate, covering the mixture with concentrated sulfuric acid, and distilling, a brown distillate is obtained (as with a chloride), which, however, consists of bromine, and contains no chromium:

$$Cr_2O_7^{--} + 6\,Br^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 7\,H_2O + 3\,Br_2\uparrow$$

On adding dilute sodium hydroxide to the distillate, a colorless (or sometimes a faint yellow) solution is obtained which, after being acidified with sulfuric acid, does not give the chromium reaction with

dilute sulfuric acid and hydrogen peroxide, but merely turns brown owing to the liberation of free bromine (difference from chlorine).

11. **Potassium Permanganate** oxidizes hydrobromic acid more readily than it does hydrochloric acid and less readily than it does hydriodic acid.

DETECTION OF BROMINE IN NON-ELECTROLYTES

The procedure is exactly the same as was given in the test for chlorine in a non-electrolyte (see p. 304).

FREE BROMINE

Free bromine (which may be obtained by the oxidation of hydrobromic acid) is a brown liquid at ordinary temperatures, and dissolves in water, forming a colored solution. Bromine boils at 63°, and evaporates rapidly at ordinary temperatures. Bromine vapors are brownish red and very poisonous. The cold, saturated solution of bromine contains 2 to 3 per cent of dissolved bromine. Concentrated hydrochloric acid at the ordinary temperatures dissolves much more bromine; the saturated solution containing about 13 per cent of the substance is an efficient oxidizing agent. Alcohol, ether, carbon bisulfide, carbon tetrachloride, and chloroform dissolve bromine very readily. Bromine is so much more soluble in these last three solvents, which are heavier than water and do not mix with it to any extent, that the greater part of the bromine can be removed by shaking the aqueous solution with a much smaller volume of the other liquid solvent. Bromine water, like chlorine water, is decomposed by standing in the light; by shaking with mercury the free bromine is taken up and the presence of hydrobromic acid is shown by the acid reaction. Hence the detection of hydrobromic acid in the presence of bromine is accomplished in precisely the same way as was described for the detection of hydrochloric acid in the presence of free chlorine (cf. p. 306).

Bromine, like chlorine, acts as a strong bleaching agent (oxidizing the color) and combines directly with metallic mercury, forming insoluble mercurous bromide.

Bromine acts upon solutions of alkali hydroxides exactly as chlorine does:

(*a*) In a cold dilute solution:

$$Br_2 + 2\ OH^- \rightarrow Br^- + BrO^- + H_2O$$

(*b*) On warming:

$$3\ Br_2 + 6\ OH^- \rightarrow 5\ Br^- + BrO_3^- + 3\ H_2O$$

(*c*) Upon adding ammonia:

$$3\ Br_2 + 8\ NH_3 \rightarrow 6\ NH_4Br + N_2\uparrow$$

HYDRIODIC ACID, HI

Occurrence. — Iodine occurs in nature as the iodide and as the iodate, most frequently as the former, accompanying (in small amounts) chlorine and bromine, *e.g.*, in the ocean, in mineral waters, etc.

Preparation. — Pure hydrogen iodide can be obtained by the action of an acid iodide upon water:

$$PI_3 + 3\ H_2O \rightarrow H_3PO_3 + 3\ HI$$

If we attempt to prepare hydriodic acid by the action of sulfuric acid upon iodides, even from dilute solutions, it is more difficult than in the case of hydrobromic acid to obtain a pure product, on account of the strong reducing power of hydriodic acid. The hydriodic acid thus obtained always contains a large amount of iodine, together with the reduction products of sulfuric acid, the latter varying in composition according to the concentration of the acid employed and of the iodide solution. Thus, with considerable concentrated sulfuric acid, sulfur dioxide is obtained:

$$2\ NaI + 3\ H_2SO_4 \rightarrow 2\ NaHSO_4 + 2\ H_2O + SO_2\uparrow + I_2$$

But if considerable iodide is present, the sulfuric acid is reduced to sulfur and finally to hydrogen sulfide:

$$6\ KI + 7\ H_2SO_4 \rightarrow 6\ KHSO_4 + S + 4\ H_2O + 3\ I_2$$

$$8\ KI + 9\ H_2SO_4 \rightarrow 8\ KHSO_4 + H_2S\uparrow + 4\ H_2O + 4\ I_2$$

A dilute solution of hydriodic acid can be obtained by passing hydrogen sulfide into a suspension of iodine in water:

$$H_2S + I_2 \rightarrow 2\ HI + S$$

It can also be made by heating an alkali iodide with phosphoric acid and absorbing the vapors in cold water or by the action of phosphorus, iodine, and water:

$$2\ P + 5\ I_2 + 8\ H_2O \rightarrow 2\ H_3PO_4 + 10\ HI$$

Properties. — Pure hydrogen iodide is a colorless gas of suffocating odor with critical temperature 150° and critical pressure 71 atmospheres. The solid melts at - 51° and boils at −35.5°. When heated, hydrogen iodide begins to dissociate into hydrogen and iodine at 180°, but at 1000° the dissociation is only 29 per cent. With water it forms a constant-boiling mixture at 127°, the mixture contains 57 per cent HI and has a density of 1.71. Solutions of higher density fume on exposure to the air.

The aqueous solution of hydriodic acid is even more difficult to keep than a solution of hydrobromic acid; it soon turns brown, owing to the separation of iodine:

$$4\ HI + O_2\ (air) \rightarrow 2\ H_2O + 2\ I_2$$

If hydrogen sulfide is conducted into the brown solution, it is decolorized, with separation of sulfur:

$$I_2 + H_2S \rightarrow 2\ HI + S$$

Owing to the extremely slight ionization of complex mercuric iodide anions, hydriodic acid is capable of dissolving mercury, which is considerably below hydrogen

in the electromotive series (cf. pp. 43 and 47):

$$Hg + 4\,HI \rightarrow H_2[HgI_4] + H_2\uparrow$$

Hydriodic acid (like hydrochloric and hydrobromic acids) is oxidized by peroxides, nitrates, nitrites, chromates, etc., with separation of iodine; in this case the oxidation of the hydriodic acid takes place so readily that a very dilute solution is oxidized by nitrous and chromic acids even in the cold.

Hydriodic acid is a monobasic acid; its salts are called iodides. It is a strong acid and the dilute aqueous solutions are almost completely ionized.

The solubilities of the iodine compounds are analogous to the corresponding bromine and chlorine compounds. The cuprous, silver, mercury, and palladium salts are much less soluble than the corresponding chlorine or bromine compounds.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** (1 : 10) attacks the iodides of the alkalies perceptibly, but only on warming.

2. **Concentrated Sulfuric Acid** reacts in the cold (cf. p. 315).

3. **Silver Nitrate** produces a yellow, curdy precipitate of silver iodide, insoluble in nitric acid, and only slightly soluble in ammonia, but readily soluble in potassium cyanide and sodium thiosulfate.

Treatment with ammonia causes the silver iodide to assume a much lighter color.

By the action of chlorine gas, silver iodide is readily changed into silver chloride:

$$2\,AgI + Cl_2 \rightarrow 2\,AgCl + I_2$$

On the other hand, if chloride or bromide of silver is treated with potassium iodide solution it will be changed into silver iodide:

$$AgCl + KI \rightarrow KCl + AgI$$
$$AgBr + KI \rightarrow KBr + AgI$$

This apparently anomalous behavior is easy to explain. As its position in the electromotive series shows, free chlorine can displace bromine or iodine in its salts; it has a greater tendency to be reduced to chloride ions. On the other hand, silver iodide is far less soluble than silver bromide and the latter is less soluble than silver chloride, and, for this reason alone, iodide ions will replace chloride or bromide ions in the case of the silver salts.

4. **Bromine Water** reacts with iodide ions in the same way that chlorine does.

The following test is capable of detecting 0.1 γ of iodine present as iodide. It depends upon the oxidation of the original iodide to iodate, the removal of the excess oxidizer by its reaction with phenol, or with formic acid, and reaction of the iodate with some added iodide and acid.

$$I^- + 3\,Br_2 + 3\,H_2O \rightarrow IO_3^- + 6\,H^+ + 6\,Br^-$$
$$3\,Br_2 + C_6H_5OH \rightarrow C_6H_2Br_3OH + 3\,HBr$$
$$Br_2 + HCO_2H \rightarrow 2\,HBr + CO_2$$
$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,H_2O + 3\,I_2$$

The interesting part of this test is that iodide is used to detect iodine that was originally present as iodide. Place 1 drop of the neutral solution to be tested in a tiny porcelain crucible, add 1 drop of saturated bromine water, heat carefully, and remove the excess bromine by adding a small crystal of phenol (or a drop of 80 per cent formic acid). Cool, make acid, and add 1 drop of 5 per cent potassium iodide solution and 1 drop of starch solution. A blue color shows the presence of iodine.

5. **Chlorine Water** sets free iodine from iodides,

$$2\,KI + Cl_2 \rightarrow 2\,KCl + I_2$$

which colors carbon disulfide reddish violet, or starch-paste blue.

Upon adding an excess of chlorine water, the violet color disappears, the iodine being oxidized to colorless iodic acid:

$$I_2 + 6\,H_2O + 5\,Cl_2 \rightarrow 10\,HCl + 2\,HIO_3$$

6. **Cupric Salts** are reduced by iodides; a brownish mixture of cuprous iodide and iodine usually separates out although the cuprous iodide remains in solution as CuI_4^{--} if considerable iodide is present:

$$2\,Cu^{++} + 4\,I^- \rightarrow \mathbf{Cu_2I_2} + I_2$$

If sulfurous acid, sodium thiosulfate, or ferrous sulfate is then added to the solution, a nearly white deposit of cuprous iodide is obtained, owing to the free iodine being changed to hydriodic acid by the reducing agent:

$$SO_3^{--} + H_2O + I_2 \rightarrow SO_4^{--} + 2\,H^+ + 2\,I^-$$

$$2\,S_2O_3^{--} + I_2 \rightarrow S_4O_6^{--} + 2\,I^-$$

7. **Lead Salts** precipitate yellow lead iodide, soluble in considerable hot water and forming a colorless solution which deposits gold-yellow plates of PbI_2 on cooling.

8. **Mercuric Chloride** produces scarlet mercuric iodide, soluble in an excess of potassium iodide:

$$Hg^{++} + 2\,I^- \rightarrow \mathbf{HgI_2}$$

$$\mathbf{HgI_2} + 2\,I^- \rightarrow [HgI_4]^{--}$$

If a solution of an alkali iodide is treated with ammonia and a little potassium hydroxide and then with a few drops of mercuric chloride, a reddish brown precipitate of dimercuricammino-iodide is obtained. This is a sensitive reaction.

9. **Nitrous Acid.** — If a dilute solution of an iodide is treated with nitrous acid, iodine separates out and the solution becomes yellow or brown in color (difference from chlorides and bromides):

$$2\,HNO_2 + 2\,HI \rightarrow 2\,NO + I_2 + 2\,H_2O$$

This extremely sensitive reaction is best performed as follows:

Prepare a solution of nitrous acid in concentrated sulfuric acid (nitrosyl sulfuric acid) by heating arsenic trioxide with nitric acid (density 1.30–1.35) and conducting the gases evolved (NO_2 and NO) into sulfuric acid (density 1.75–1.80):

$$As_2O_3 + 2\,HNO_3 \rightarrow As_2O_5 + H_2O + NO_2\uparrow + NO\uparrow$$

$$2\,SO_2\begin{matrix}/OH\\\backslash OH\end{matrix} + NO_2 + NO \rightarrow H_2O + 2\,SO_2\begin{matrix}/OH\\\backslash O(NO)\end{matrix}$$

This solution of nitrosylsulfuric acid is sometimes called "nitrose." It can be kept for some time, but water decomposes it into nitrous and sulfuric acids:

$$SO_2\begin{matrix}/OH\\\backslash ONO\end{matrix} + HOH \rightarrow H_2SO_4 + HNO_2$$

Treat the solution to be tested with a few drops of *nitrose* and shake with a little carbon disulfide or chloroform; if an iodide is present, iodine is liberated, which colors the carbon disulfide or chloroform violet.

10. **Palladous Chloride** (it is best to use sodium chloropalladite) precipitates black palladous iodide from dilute solutions of an iodide (difference from chlorine and bromine),

$$Na_2[PdCl_4] + 2\,KI \rightarrow 2\,NaCl + 2\,KCl + \mathbf{PdI_2}$$

which is readily soluble in an excess of potassium iodide.

11. **Potassium Dichromate,** in the presence of dilute sulfuric acid causes the separation of iodine from dilute iodide solutions in the cold; the iodine can be more easily recognized by shaking the solution with chloroform or carbon disulfide (difference from bromine):

$$Cr_2O_7^{--} + 6\,I^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 7\,H_2O + 3\,I_2$$

By heating a mixture of solid iodide and solid potassium dichromate with concentrated sulfuric acid, iodine is set free (according to the above equation), which distils over, and can be condensed in the receiver. No chromium is carried over by this reaction (difference from chlorine).

12. **Potassium Permanganate** oxidizes hydriodic acid more readily than it acts upon hydrobromic or hydrochloric acids. The oxidation will take place in dilute acetic acid solutions containing considerable sodium acetate.

DETECTION OF IODINE IN NON-ELECTROLYTES

The method is the same as described for detecting chlorine in non-electrolytes (see p. 304).

FREE IODINE

Free iodine forms scales resembling graphite in appearance; its density is 4.94 at 17°. It melts at 114° (at the same temperature as sulfur), but begins to volatilize at ordinary temperatures, and is completely transformed into violet vapors at 200°.

Iodine is only slightly soluble in water (100 parts of water dissolve 0.02 part of iodine) but is soluble to a considerable extent in alcohol and ether, forming brown solutions, and it is much more soluble in carbon disulfide, carbon tetrachloride, and chloroform; practically all the iodine can be removed from an aqueous solution by shaking a few times with either of these solvents (cf. p. 14). Iodine is very soluble in hydriodic acid, or in a solution of an alkali iodide, forming tri-iodide ions:

$$I^- + I_2 \rightleftarrows I_3^-$$

The solution of the tri-iodide shows all the reactions of free iodine, but the vapor tension of the iodine is much less than in a solution of pure water because only a little free iodine is actually present at any one time.

Commercial iodine always contains water, chlorine, bromine, and often cyanogen (cyanogen iodide) as impurities.

An aqueous solution of iodine is a weak oxidizing agent. If hydrogen sulfide is passed through an aqueous solution of iodine, it becomes colorless and turbid, owing to the separation of sulfur:

$$H_2S + I_2 \rightarrow 2\,HI + S$$

Solid iodine is not acted upon at ordinary temperatures by hydrogen sulfide; heat is necessary to produce the endothermic hydriodic acid.

In aqueous solution the necessary heat energy is furnished by the solution of the hydriodic acid formed in water. The fact that solid iodine is not acted upon by hydrogen sulfide, while it decomposes arsine, is utilized in the preparation of hydrogen sulfide containing no arsenic from pyrites containing arsenic (cf. p. 152). The mixture of hydrogen sulfide and arsine is passed over iodine, and only the arsine is removed.

Reactions in the Wet Way

1. **Sodium Thiosulfate** decolorizes iodine solutions, forming sodium tetrathionate and sodium iodide:

$$2\,S_2O_3^{--} + I_2 \rightarrow S_4O_6^{--} + 2\,I^-$$

Chlorine and bromine react in exactly the same way upon sodium thiosulfate solutions when they are not present in excess. In the latter case the reaction goes further and the tetrathionate is oxidized to sulfate and sulfuric acid with deposi-

tion of sulfur, and the sulfur itself is gradually oxidized to sulfuric acid by the halogens:

$$2\,S_4O_6^{--} + 12\,H_2O + 8\,Cl_2 \rightarrow 16\,Cl^- + 6\,SO_4^{--} + 24\,H^+ + 2\,S$$

$$2\,S + 8\,H_2O + 6\,Cl_2 \rightarrow 16\,H^+ + 2\,SO_4^{--} + 12\,Cl^-$$

Other weak oxidizing agents, such as ferric and cupric salts, act upon thiosulfate similarly to iodine (see Thiosulfuric Acid).

2. **Starch Paste.** — Free iodine colors starch paste blue, but only in the presence of hydriodic acid or a soluble iodide.

Opinions differ concerning the composition of the blue "iodide of starch." Some hold that it is a compound; others regard it as a solid solution.* According to Mylius,† iodide of starch is the hydriodic acid compound of an iodine addition-product of starch, containing about 18 per cent iodine, corresponding to the formula $[C_{24}H_{40}O_{20}I]_4 \cdot HI$. This compound acts as an acid. If iodide of starch is produced, in a neutral solution, in the presence of iodides, a salt of the above acid is formed, of which Mylius isolated the barium salt. Iodide of starch, then, can be regarded as a double salt, similar to carnallite, $MgCl_2 \cdot KCl \cdot 6\,H_2O$. In dilute solutions it must be dissociated into its components, *e.g.*, the potassium salt

$$[C_{24}H_{40}O_{20}I]_4 \cdot KI \rightleftarrows 4\,[C_{24}H_{40}O_{20}I] + KI$$

and if we assume that the compound $C_{24}H_{40}O_{20}I$ is colorless, the aqueous solution of starch iodide will be colorless; but on increasing the concentration of the alkali iodide, the double salt will be less dissociated and the blue color of the undissociated compound will appear, which corresponds with the facts. If a dilute aqueous iodine solution (obtained by shaking iodine with water) is added drop by drop to a dilute aqueous starch solution, a blue color will appear at the spot where the two solutions first come in contact, but this color will disappear on stirring. If some potassium (or other) iodide is added to the colorless solution of the starch and iodine, a permanent blue coloration will at once appear.‡

The temporary appearance of the blue color, immediately on adding the iodine solution, is probably due to the fact that the iodine first forms a substitution product with the starch, setting free hydriodic acid, which furnishes the conditions for the formation of the iodide of starch.

The fact that a starch solution containing an iodide is much more sensitive than one in pure water has been known for a long time.

DETECTION OF HYDROCHLORIC, HYDROBROMIC, AND HYDRIODIC ACIDS IN THE PRESENCE OF ONE ANOTHER

Method A

The solution to be tested should contain the alkali salts of the above acids. Half of this solution is taken for the bromide and iodide test, the other half being retained for the chloride test.

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* Küster, *Ann.*, **283**, 689 (1894), C. O. Harz, *Chem. Zentr.*, **1898**, I, 1018; Andrews and Götsch, *J. Am. Chem. Soc.*, **24**, 865 (1906); Padra and Savori, *Chem. Zentr.*, **1905**, I, 1593; Katyama, *Z. anorg. Chem.*, **58**, 209 (1907).

† Mylius, *Ber.*, **20**, 688, and C. Lonnes, *Z. anal. Chem.*, **33**, 409.

‡ The blue color disappears on heating the solution, but reappears on cooling.

(*a*) *Detection of Bromine and Iodine*

1. Acidify the solution with dilute sulfuric acid, add a little carbon disulfide, or chloroform, a drop of chlorine water, and shake. If *iodine* is present (even in the presence of bromine), the carbon disulfide will be colored reddish violet.

To detect *bromine* shake repeatedly after the addition of small portions of chlorine water, until the reddish violet color has disappeared, showing that the iodine has been completely oxidized to iodic acid; the brown color of the bromine dissolved in the carbon disulfide will then appear and become a pale yellow on further addition of chlorine water.

2. Instead of using chlorine water, it is often better to test for iodine (especially when only small amounts are present, as in mineral waters) with nitrous acid. Slightly acidify the solution to be tested for iodine and bromine with dilute sulfuric acid, add carbon disulfide and a few drops of a solution of nitrous acid in sulfuric acid, and shake the mixture. If the carbon disulfide is colored reddish violet, iodine is present. Pour off the aqueous solution (through a moistened filter, in order to remove any suspended drops of colored carbon disulfide), add chlorine water, and shake the solution with fresh carbon disulfide. If the latter now assumes a brown color, bromine is present.

(*b*) *Detection of Chlorine*

The simplest way of separating chlorine from bromine and iodine is by fractional precipitation with silver nitrate. If the solution containing salts of the three halogens is treated with dilute silver nitrate, drop by drop, the iodide will be first precipitated as yellow silver iodide, then the bromide as a pale yellow silver salt, and finally the chloride as pure white silver chloride. To separate the chlorine from the other two halogens, acidify a little of the solution to be tested with nitric acid, add a drop of dilute silver nitrate solution (1 : 100), shake, and boil the mixture, which causes the precipitate to collect together. If bromine or iodine is present, the precipitate is yellow. Filter off the precipitate and again treat with the dilute silver nitrate, etc., until a pure white precipitate of silver chloride is obtained, if chlorine is present.

By filtering off the precipitate it is easy to tell whether it is pure white, for the slightest tinge of yellow will show against the white paper.

Method B

This method of analysis is based upon the different degrees of readiness with which the iodide, bromide, and chloride ions are oxidized by 1 per cent potassium permanganate solution. In a dilute solution containing a little acetic acid and considerable sodium acetate, an iodide is immediately oxidized with liberation of iodine, which can be removed from the solution by shaking with a solvent which is immiscible with water (cf. p. 14). Under these conditions an appreciable quantity of bromide or chloride ions is not oxidized in the time required for the necessary operations with an iodide. When the concentration of the hydrogen ions is increased, by the addition of a prescribed quantity of sulfuric acid, the bromide is oxidized very rapidly while the rate of the corresponding reaction with chloride ions is so slow that scarcely any free chlorine is formed. The solution may even be boiled without losing more than a small fraction of the chloride ions originally present.

The increase in the oxidizing power of the permanganate upon the addition of hydrogen ions is a direct fulfillment of the mass-action principle (p. 45). In the

reaction between permanganate and halogen ions, hydrogen ions are required,

$$2\ MnO_4^- + 6\ I^- + 8\ H^+ \rightarrow 2\ MnO_2 + 4\ H_2O + 3\ I_2$$

or

$$2\ MnO_4^- + 10\ I^- + 16\ H^+ \rightarrow 2\ Mn^{++} + 8\ H_2O + 5\ I_2$$

The permanganate will be reduced only to the quadrivalent condition, and manganese dioxide will be precipitated, when the supply of hydrogen ions is limited, but bivalent managanous cations will be formed to a greater extent when more acid is present.

In carrying out this method of analysis, it is very important that the directions should be closely followed as regards the quantities of acid added.

Procedure. — If the solution to be tested is acid, add sodium carbonate solution drop by drop until the solution no longer gives a decided red color to blue litmus paper. If too much sodium carbonate is added accidentally, add dilute nitric acid, drop by drop, until a very faint acid test is obtained in the well-stirred liquid. Then add 8 ml of normal sodium acetate solution and 2 ml of 6-normal acetic acid, and filter if any precipitate is formed. Add 3 ml of chloroform and 1 per cent permanganate solution, 1 ml at a time, until the aqueous solution after being vigorously shaken shows the pink color of permanganate. If an iodide is present, the chloroform will now be colored purple by the presence of free iodine.

Pour the mixture through a moistened filter to remove the chloroform and precipitated manganese dioxide; the wetting with water serves to prevent chloroform passing through the pores of the paper. Shake the filtrate, if necessary, with fresh portions of chloroform to extract all the iodine from the aqueous solution (cf. p. 14), filtering through a fresh filter each time.

When all the iodine has been removed, transfer the solution to a separatory funnel; add 3 ml of fresh chloroform, 5 ml of 6-normal sulfuric acid, and 1 ml of the dilute permanganate, unless an excess of the last-mentioned reagent is already present. Shake vigorously, and then allow the chloroform to separate out beneath the water. If bromine is present, the chloroform will be colored yellow or orange.

Carefully remove the chloroform with the aid of the separatory funnel and transfer the aqueous solution to a porcelain dish. Add from 5 to 20 ml of dilute permanganate, according to the amount of bromide probably present, and boil the mixture about five minutes, or until the volume of the solution has been reduced to 10 ml. Filter off the manganese dioxide precipitate; and, if the solution is still pink, add sulfurous acid drop by drop until it is colorless. Boiling the solution serves to oxidize the last traces of bromine ions present without oxidizing chlorine ions to any extent. The excess of permanganate reacts with manganous ions (formed by reduction of the permanganate) to form manganese dioxide,

$$2\ MnO_4^- + 3\ Mn^{++} + 2\ H_2O \rightarrow 5\ MnO_2 + 4\ H^+$$

but the presence of hydrogen ions interferes with this reaction, in accordance with the mass-action law. Consequently, either owing to the fact that there is a deficiency of manganous ions in the solution or because the concentration of the hydrogen ions is too great, it is often necessary to add sulfurous acid to reduce the last traces of permanganate ion.

$$2\ MnO_4^- + 5\ SO_3^{--} + 6\ H^+ \rightarrow 2\ Mn^{++} + 5\ SO_4^{--} + 3\ H_2O$$

Dilute the solution to 100 ml, filter if necessary, add 20 ml of 6-normal nitric acid and a little silver nitrate solution. A curdy precipitate of silver chloride is formed if a chloride is present.

Remark. — The above method of separation is capable of giving excellent results. A solid substance can be tested for chloride, bromide, and iodide after first heating it with phosphoric acid and collecting the distillate. If about 2 g of solid, 25 ml of water, and 10 ml of 85 per cent phosphoric acid are used, all the iodine, bromine, and chlorine will pass into the distillate. If any oxidizing agent is present, however, free iodine, free bromine, and free chlorine will be formed in the order named. The free halogen can be removed by shaking the distillate with chloroform (cf. p. 321). If free chlorine is formed, it will dissolve in the chloroform. Iodine and bromine are recognized by the color they impart to the chloroform and chlorine and bromine by the liberation of iodine from potassium iodide. After the removal of the free halogen, the distillate may be tested for hydriodic, hydrobromic, and hydrochloric acids as described on pages 320, 321. By distilling with phosphoric acid, halogen is obtained even from chlorates and bromates if a reducing agent is present.

DETECTION OF HALOGEN IN THE PRESENCE OF CYANIDE

Conduct carbon dioxide through the slightly alkaline, boiling solution until the escaping gas no longer gives any turbidity when passed into a nitric acid solution of silver nitrate.

The carbon dioxide may be prepared in a Kipp generator from marble and dilute hydrochloric acid and washed with sodium bicarbonate solution. The carbonic acid expels the weaker hydrocyanic acid from its salts (cf. p. 11). Owing to the very poisonous nature of hydrocyanic acid, the expulsion of the gas should take place under a good hood.

After the removal of the hydrocyanic acid, test the solution in the usual way for halogens.

HYDROCYANIC ACID (PRUSSIC ACID), HCN

Occurrence. — The compound of hydrogen with the univalent cyanide radical, CN^-, occurs to some extent in nature. It is found in all parts of a tree growing in Java (*Pangium edule*), particularly in the seed kernels. Its compounds are found in many plants as a glucoside (amygdalin), which yields, on hydrolysis, a carbohydrate, benzaldehyde, and prussic acid:

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2\,H_2O \rightarrow 2\,C_6H_{12}O_6 + \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCN$$

Amygdalin is found in bitter almonds, in the fruit kernels of cherries, apricots, peaches, etc., and in the leaves of the cherry laurel (*Prunus laurocerassus*). It is usually accompanied by a ferment, so that, on macerating the parts of the plant which contain the amygdalin, an aqueous solution of prussic acid is obtained (bitter-almond water).

Preparation. — If ammonia is passed over glowing carbon, ammonium cyanide is formed; so that this salt, as well as other cyanogen compounds, is found in the "gas-water" obtained by the dry distillation of coal.

Hydrocyanic acid may also be prepared by adding acid to many cyanogen compounds. If yellow prussiate of potash is treated with dilute sulfuric acid and distilled, prussic acid is evolved, which, after standing over solid calcium chloride, may be obtained in the anhydrous condition as a colorless, exceedingly poisonous liquid, smelling of bitter almonds, and boiling at 26.5° C:

$$2\,K_4[Fe(CN)_6] + 6\,H_2SO_4 \rightarrow 6\,KHSO_4 + K_2Fe[Fe(CN)_6] + 6\,HCN$$

The most convenient method for preparing anhydrous hydrogen cyanide* consists in allowing a mixture of equal volumes of sulfuric acid and water to drop upon sticks of 98 per cent potassium cyanide. Hydrogen cyanide is evolved, contaminated with traces of water which can be removed by allowing the liquid to stand over solid calcium chloride.

Properties. — Hydrogen cyanide is a clear mobile liquid which boils at 26.5° and freezes at −15°. It burns with a purple flame to form H_2O, CO_2, and N_2. It mixes in all proportions with water, alcohol, and ether.

Aqueous hydrocyanic acid cannot be kept indefinitely; a brown deposit soon appears, and ammonium formate is formed:

$$HCN + 2\,HOH \rightarrow HCO_2NH_4$$

If a little mineral acid is added to the aqueous solution, it may be kept much longer; but, even then, ammonia and formic acid will be formed after a long time. Cold concentrated hydrochloric acid converts hydrocyanic acid into formamide, $HCN + H_2O \rightarrow HCONH_2$, but on warming this compound is decomposed into carbon monoxide and ammonia.

Hydrocyanic acid in aqueous solution is a very poor conductor of electricity; in other words, it is a very weak acid, and is ionized only to a slight extent. The

* J. Wade and L. Panting, *Proc. Chem. Soc.*, **190**, 49 (1897–8).

ionization constant is 7×10^{-10} at 18°. In 0.1-normal solution it is only 0.006 per cent ionized.

The salts of hydrocyanic acid, the cyanides, are very similar in their properties to the corresponding halogen compounds, but are distinguished by their ability to form stable complex salts, which contain scarcely any cyanide ions in aqueous solution, and consequently do not give some of the reactions for hydrocyanic acid.

Solubility of Cyanides. — The cyanides of the alkalies and alkaline earths are readily soluble in water, but hydrolysis (p. 52) takes place to a considerable extent:

$$CN^- + H_2O \rightarrow OH^- + HCN$$

Since hydrocyanic acid is only slightly ionized, the aqueous solution of an alkali cyanide behaves like a solution of alkali hydroxide containing free prussic acid; the odor of the latter can be easily detected. The salts of hydrocyanic acid are decomposed by acids, even by weak carbonic acid.

The remaining cyanides, with the exception of mercuric cyanide, are insoluble in water.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** decomposes solutions of all soluble cyanides, with the exception of mercuric cyanide, setting free hydrocyanic acid in the cold (recognizable by its odor). Danger!

The insoluble cyanides are decomposed by dilute sulfuric acid only on warming.

2. **Concentrated Sulfuric Acid** decomposes all cyanides on warming, the complex cyanides as well as the simple ones. The metals are then obtained in the form of acid sulfates, the carbon of the cyanogen is changed to carbon monoxide, and the nitrogen into ammonium bisulfate:

$$Ni(CN)_2 + 3\,H_2SO_4 + 2\,H_2O \rightarrow NiSO_4 + 2\,NH_4HSO_4 + 2\,CO\uparrow$$

With mercuric cyanide, besides carbon monoxide, sulfur dioxide and carbon dioxide are obtained; for mercuric cyanide is decomposed at the temperature of boiling sulfuric acid into mercury and cyanogen and the former dissolves in the hot sulfuric acid, with formation of mercuric sulfate and evolution of sulfur dioxide:

$$Hg(CN)_2 + 6\,H_2SO_4 \rightarrow 2\,NH_4HSO_4 + Hg(HSO_4)_2 + CO\uparrow + CO_2\uparrow + SO_2\uparrow + SO_3\uparrow$$

3. **Silver Nitrate.** — If silver nitrate is added to a solution of an alkali cyanide drop by drop, a precipitate is formed on the addition of each drop, which, however, redissolves on stirring the liquid, for silver cyanide is soluble in an excess of alkali cyanide:

$$CN^- + Ag^+ \rightarrow \mathbf{AgCN}$$
$$\mathbf{AgCN} + CN^- \rightarrow [Ag(CN)_2]^-$$

The complex silver cyanide ion is decomposed by further addition of silver nitrate, being finally completely transformed into insoluble silver cyanide:

$$[Ag(CN)_2]^- + Ag^+ \rightarrow 2\ AgCN$$

Consequently the precipitation is complete only when an excess of silver nitrate is added.

Silver cyanide is insoluble in water and dilute nitric acid, perceptibly soluble in concentrated nitric acid, and readily soluble in ammonia, sodium thiosulfate, and potassium cyanide solutions. Dilute nitric acid reprecipitates silver cyanide from the solution in ammonia or potassium cyanide.

Concentrated hydrochloric acid decomposes silver cyanide, on warming, into silver chloride, with evolution of hydrocyanic acid (difference from silver chloride, bromide, or iodide).

By igniting silver cyanide, there is formed cyanogen gas, metallic silver, and brown, difficultly volatile paracyanogen, which, on further heating, is completely volatilized, leaving behind pure silver:

$$2\ AgCN \rightarrow 2\ Ag + (CN)_2 \uparrow$$

Much more certain than the silver nitrate test are the tests for hydrocyanic acid which depend upon the formation of Prussian blue or of ferric thiocyanate.

4. **Blue Starch-Iodide Solution** is decolorized by a trace of alkali cyanide and a little sulfuric acid: the iodine unites with the hydrocyanic acid to form cyanogen iodide and hydriodic acid,

$$HCN + I_2 \rightarrow CNI + HI$$

The reaction is very sensitive, but many other substances decolorize blue iodide of starch.

5. **Copper Acetate and Benzidine Acetate.** Colorless benzidine acetate is changed to a blue, quinoidal imide by oxidation (cf. pp. 113,134). The oxidation can take place by cupric salt in the presence of hydrocyanic acid:

$$Cu(C_2H_3O_2)_2 + 2\ HCN \rightarrow Cu(CN)_2 + 2\ HC_2H_3O_2$$
$$2\ Cu(CN)_2 + H_2O \rightarrow Cu_2(CN)_2 + 2\ HCN + O$$

In a tiny porcelain crucible, place 1 drop of the solution to be tested for cyanide, add 1 drop of 6 *N* sulfuric acid, and cover the crucible tightly with filter paper which has been moistened with 1 drop of a mixture of equal parts cupric acetate solution (2.86 g per liter) and benzidine acetate solution (475 ml of saturated, aqueous benzidine acetate solution diluted with 525 ml of water). A blue ring will soon form around the spot on the filter paper. As little as 0.25 γ of CN will give the test.

6. **Copper Sulfide** is dissolved by alkali cyanide solution:

$$CuS + 4\ KCN \rightarrow K_2Cu(CN)_4 + K_2S$$

Dissolve about 0.12 g of copper sulfate crystals in 100 ml of water, add a few drops of ammonia, and introduce a little hydrogen sulfide. Place a drop of the suspension of copper sulfide on filter paper, or a spot plate, and add 1 drop of the alkaline solution to be tested. The sulfide will dissolve if alkali cyanide is present.

Another way of applying the test is to moisten a piece of filter paper with an ammoniacal 0.1 per cent copper solution. Just before making the test blow a little hydrogen sulfide vapor against the paper so that it is colored a uniform yellow-brown. Place 1 drop of the alkaline solution to be tested upon the paper, and a white ring will form if cyanide is present. This test can be obtained with 1.25 γ of CN.

7. **Ferric Thiocyanate Reaction.** — Potassium thiocyanate produces a red coloration with a ferric salt, owing to the formation of slightly ionized ferric thiocyanate (cf. p. 215):

$$3\ CNS^- + Fe^{+++} \rightarrow Fe(CNS)_3$$

The cyanide, therefore, must be changed to thiocyanate in order to apply this reaction, which can be done by heating with sulfur,

$$KCN + S \rightarrow KCNS$$

or, better, by treatment with an alkaline polysulfide,

$$KCN + (NH_4)_2S_2 \rightarrow (NH_4)_2S + KCNS$$

To the concentrated solution of the cyanide (in a porcelain dish) add a little yellow ammonium sulfide and evaporate the mixture to dryness on the water-bath. Add a little hydrochloric acid and a drop of ferric chloride solution; the characteristic blood-red coloration will be produced if only traces of cyanide are present.

It is necessary to acidify in order to destroy the $(NH_4)_2S$, which would precipitate black Fe_2S_3 with $FeCl_3$ and the red coloration would not appear.

8. **Mercurous Nitrate** produces a gray precipitate of metallic mercury when added to a solution of an alkali cyanide (difference from a chloride, bromide, or iodide):

$$Hg_2^{++} + 2\ CN^- \rightarrow Hg(CN)_2 + \mathbf{Hg}$$

9. **Prussian Blue Reaction.** — Prussian blue is formed by the action of ferric salts upon potassium ferrocyanide (cf. p. 215).

$$3\ [Fe(CN)_6]^{----} + 4\ Fe^{+++} \rightarrow \mathbf{Fe_4[Fe(CN)_6]_3}$$

In order, therefore, to apply this reaction to potassium cyanide, etc., it is necessary first to transform the cyanide into potassium ferrocyanide. This may be accomplished by the addition of a ferrous salt, whereby ferrous cyanide is first formed, which dissolves in an excess of potassium cyanide, forming potassium ferrocyanide:

$$Fe^{++} + 2\ CN^- \rightarrow \mathbf{Fe(CN)_2}$$
$$\mathbf{Fe(CN)_2} + 4\ CN^- \rightarrow [Fe(CN)_6]^{----}$$

Potassium ferrocyanide is formed even more readily by the action of potassium cyanide upon ferrous hydroxide:

$$\mathbf{Fe(OH)_2} + 2\ CN^- \rightarrow \mathbf{Fe(CN)_2} + 2\ OH^-$$
$$\mathbf{Fe(CN)_2} + 4\ CN^- \rightarrow [Fe(CN)_6]^{----}$$

For the formation of the potassium ferrocyanide a little iron and considerable potassium cyanide are required. Consequently, to bring about the reaction, add a little ferrous sulfate to the alkaline solution of an alkali cyanide and boil the mixture.

Then add a little hydrochloric acid, whereby a clear solution is obtained, which gives, with a little ferric chloride, the blue precipitate. If only traces of hydrocyanic acid are present, the solution appears green at first, but, after standing some time, "flocks" of Prussian blue will be precipitated.

The Prussian blue reaction is used for the detection of nitrogen in organic substances (cf. p. 331).

Remark. — When only a trace of cyanide is present, the Prussian blue seen through yellow ferric chloride appears green. If the ferric chloride solution is diluted largely to get rid of the yellow color, the iron is then largely in colloidal solution, as a result of the formation of basic salt by hydrolysis; such a solution reacts very slowly with ferrocyanide. A more sensitive test for *traces* of ferrocyanide is obtained by adding a saturated solution of *ferrous* sulfate. Such a solution always contains enough ferric ions to give the Prussian blue test with a trace of ferrocyanide ions. When more than a trace of ferrocyanide is present, however, it is best to test with ferric chloride solution as outlined on page 327.

10. **Sodium Nitroprusside Reaction.** — If a solution of hydrocyanic acid or of an alkali cyanide is treated with a few drops of alkali nitrite solution and then with two or three drops of ferric chloride and just enough very dilute sulfuric acid to change the color of the ferric salt that forms from brown to light yellow, then upon heating to the boiling point, cooling, and adding enough ammonia to precipitate the excess of ferric ion, a filtrate is obtained which will give a violet coloration with a few drops of hydrogen sulfide water. The reaction depends upon the formation of the nitroprusside ion $[Fe(CN)_5NO]^{--}$ which gives a reddish violet color with sulfide ions.

Behavior of Mercuric Cyanide

Mercuric cyanide, $Hg(CN)_2$, is a non-electrolyte, is quite soluble in water, alcohol, and ether, and behaves quite differently from all other cyanides. All the above-mentioned reactions, with the exception of the ferric thiocyanate test, fail with this compound. Mercuric cyanide solution gives no precipitate with silver nitrate, but a readily soluble double salt is formed,

$$Hg(CN)_2 \cdot AgNO_3 \cdot 2\,H_2O$$

Similarly no precipitate is formed with ammonia, potassium iodide, alkali hydroxide, or alkali carbonate because all these reagents, under ordinary conditions, give precipitates of mercuric compounds which are soluble in potassium cyanide. Thus, for example, mercuric oxide dissolves easily in potassium cyanide:

$$HgO + 2\,KCN + H_2O \rightarrow 2\,KOH + Hg(CN)_2$$

Mercuric oxide itself is fairly soluble in mercuric cyanide:

$$HgO + Hg(CN)_2 \rightarrow O\begin{matrix}\diagup Hg - CN \\ \diagdown Hg - CN\end{matrix}$$

Hydrochloric, hydrobromic, and hydriodic acid decompose mercuric cyanide readily, but dilute sulfuric acid alone has little action upon it. In the presence of a soluble chloride, however, mercuric cyanide is decomposed easily by sulfuric acid, or even by oxalic acid or tartaric acid. If, therefore, a solution of mercuric cyanide is

treated with common salt and dilute sulfuric, oxalic, or tartaric acid, then, on subjecting the mixture to distillation, a distillate is obtained containing hydrocyanic acid which gives all the tests characteristic of this acid.

Mercuric cyanide in solution is acted upon by hydrogen sulfide or by alkali sulfides, forming mercuric sulfide and hydrocyanic acid, or one of its salts. If the black precipitate is removed by filtration, the ferric thiocyanate reaction is obtained without difficulty:

$$Hg(CN)_2 + H_2S \rightarrow HgS + 2\,HCN$$

Behavior of Cyanides on Ignition

The cyanides of the alkalies and alkaline earths fuse without decomposition when heated out of contact with the air; heated in contact with air, they absorb oxygen with avidity, forming cyanates:

$$2\,KCN + O_2 \rightarrow 2\,KCNO$$

Consequently the alkali cyanides are strong reducing agents (cf. p. 173).

The cyanides of the bivalent heavy metals are decomposed on ignition, out of contact with the air, into nitrogen and metallic carbide, the latter often being further decomposed into metal and carbon:

$$3\,Fe(CN)_2 \rightarrow Fe_3C + C + 2(CN)_2\uparrow + N_2\uparrow$$
$$Pb(CN)_2 \rightarrow Pb + 2\,C + N_2\uparrow$$

The cyanides of the trivalent metals are unknown in the free state; those of the noble metals are decomposed, by igniting, into metal and dicyanogen:

$$2\,AgCN \rightarrow 2\,Ag + (CN)_2\uparrow$$
$$Hg(CN)_2 \rightarrow Hg + (CN)_2\uparrow$$

It is a characteristic property of the cyanides of the heavy metals that they are readily soluble in alkali cyanide solutions, forming very stable complex compounds, which are to be regarded as salts of the following acids:

$$H[R^{I}(CN)_2],\quad H_2[R^{II}(CN)_4],\quad H_3[R^{III}(CN)_6]\quad \text{and}\quad H_4[R^{II}(CN)_6]$$

The first two of the above acids are so unstable that they are decomposed, as soon as they are set free, into hydrocyanic acid and cyanide:

$$H[R(CN)_2] \rightarrow HCN + RCN$$
$$H_2[R(CN)_4] \rightarrow 2\,HCN + R(CN)_2$$

Consequently all cyanides which are derived from these acids evolve hydrocyanic acid when treated with dilute hydrochloric or sulfuric acid in the cold. Such compounds are:

$K[Ag(CN)_2]$, $K[Au(CN)_2]$, $K_2[Ni(CN)_4]$, $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, etc.

These salts must be regarded as complex compounds (p. 27), for their aqueous solutions contain almost no heavy metal ions; they are not precipitated by caustic alkali, alkali carbonate, or ammonia. From this fact it follows that the oxides of these metals are soluble in cyanides of the alkalies, forming the following complex salts:

$$Ag_2O + 4\,CN^- + H_2O \rightarrow 2\,OH^- + 2\,[Ag(CN)_2]^-$$
$$NiO + 4\,CN^- + H_2O \rightarrow 2\,OH^- + [Ni(CN)_4]^{--}$$
$$ZnO + 4\,CN^- + H_2O \rightarrow 2\,OH^- + [Zn(CN)_4]^{--}$$
$$CdO + 4\,CN^- + H_2O \rightarrow 2\,OH^- + [Cd(CN)_4]^{--}$$

Hydrogen sulfide decomposes the silver and cadmium salts without difficulty, the zinc salt slightly, and the nickel salt not at all.

The acids of the general formula $H_3[R^{III}(CN)_6]$ and $H_4[R^{II}(CN)_6]$ are, in contrast with the above acids, quite stable in the free state, and can be usually obtained, without the loss of hydrocyanic acid, by acidifying a solution of one of their salts with cold dilute mineral acid; but, on warming the acid solution, hydrocyanic acid is given off.

As typical representatives of these acids we have ferrocyanic, ferricyanic, and cobalticyanic acids.*

Ferrocyanic and ferricyanic acids will be discussed separately; but before doing so a brief description will be given of cyanogen itself.

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* Cobaltocyanic acid is extremely unstable, like mangano- and manganicyanic acids. Its salts evolve HCN when treated with cold, dilute, mineral acids.

CYANOGEN

This compound is obtained by heating the cyanides of the noble metals, as a colorless gas with a disagreeable odor; it burns with a reddish flame, and is soluble in water (25 parts water dissolve 100 parts of cyanogen). The aqueous solution cannot be kept very long, for brownish flocks separate out little by little (azulmic acid, $C_4H_5N_5O$) and the solution then contains ammonium cyanide, ammonium carbonate, ammonium oxalate, and urea.

Just as chlorine acts upon caustic alkalies, forming a chloride and a hypochlorite, so cyanogen reacts with them, forming a cyanide and a cyanate:

$$Cl_2 + 2\ KOH \rightarrow KCl + H_2O + KOCl$$
$$(CN)_2 + 2\ KOH \rightarrow KCN + H_2O + KOCN$$

On conducting hydrogen sulfide into a solution of cyanogen, a red, crystalline precipitate of hydrorubianic acid is obtained: $(CN)_2 + 2\ H_2S \rightarrow (CSNH_2)_2$. (Cf. p. 137.)

DETECTION OF NITROGEN IN ORGANIC SUBSTANCES
(*Lassaigne.*)

If a little nitrogenous, organic substance is placed with some metallic sodium in a small glass tube which is closed at one end, and the tube is heated till the glass begins to soften, then the nitrogen and some of the carbon of the organic substance will combine with sodium to form sodium cyanide. After heating for two minutes, plunge the hot end of the glass tube in a little water, whereby the glass breaks and the contents of the tube are immediately wet by water. Filter off the alkaline solution containing the sodium cyanide from the residual carbon and glass splinters, add a little ferrous sulfate solution, and boil. Finally add a few drops of ferric chloride solution and enough hydrochloric acid to neutralize the alkali. If nitrogen was present in the original substance, Prussian blue is now obtained.

Remark. — Certain nitrogenous substances are decomposed with evolution of nitrogen before the temperature required for the cyanide formation is reached,* and thus the nitrogen escapes the Lassaigne reaction; in other cases the experiment fails on account of the extreme volatility of the organic substance.†

According to E. A. Kehrer,‡ the Lassaigne reaction always gives positive results if the sodium is first heated by itself and then brought in contact with the vapors of the organic material. The experiment is carried out in a small tube, drawn out at the closed end, such as used for the arsenic test (cf. Fig. 13, p. 154). Place the substance in the constricted part of the tube and then, in the wider part, just before the constriction is reached, introduce a small piece of sodium which has been rolled between dry fingers and freed from petroleum by touching it to filter paper. Heat the sodium until it glows and then, by means of another small flame, heat the substance

* Gräbe, *Ber.*, **17**, 1178 (1884).

† Feist, *Ber.*, **35**, 1559 (1902).

‡ *Ber.*, **35**, 2523 (1902).

to be tested so that it melts and the vapors just rise up to the glowing sodium but hardly reach through it. By taking away the small flame, the vapors can be made to condense and be driven toward the glowing sodium again. Otherwise, carry out the test exactly as described above.

For the detection of *traces* of nitrogen it is best not to add any ferric chloride, but to add a saturated solution of ferrous sulfate, after adding the acid (cf. p. 328).

DETECTION OF HYDROCYANIC ACID IN THE PRESENCE OF HALOGEN ACID, FERROCYANIC, FERRICYANIC, AND THIOCYANIC ACIDS

Hydrocyanic acid is by far the weakest of all the above acids (cf. p. 16) and it alone is expelled from its salts by means of carbonic acid at the temperature of boiling water.

Place the solution to be tested in a small Erlenmeyer flask, add 0.6 to 1 g of $NaHCO_3$, and close the flask with a two-hole rubber stopper. Insert through one of the holes in the stopper a piece of glass tubing that reaches nearly to the bottom of the flask and serves for the introduction of the carbon dioxide gas; through the other hole insert a piece of tubing that reaches only to the bottom of the rubber stopper and serves for the escape of the gas. Pass carbon dioxide gas (cf. p. 323), through the liquid in the flask, gradually heat to boiling, and conduct the escaping vapors into silver nitrate solution which has been acidified with nitric acid.

If cyanide is present in the original solution, a white precipitate of silver cyanide is formed in the silver nitrate solution within a short time. To confirm the test, decant off the solution from the precipitate and wash it a few times by decantation with water. Cover the precipitate with a little yellow ammonium sulfide, warm, and filter. Evaporate the filtrate to a small volume and treat with a little hydrochloric acid and a few drops of ferric chloride solution. A red color, due to ferric thiocyanate, proves the presence of cyanide.

FERROCYANIC ACID, $H_4[Fe(CN)_6]$

Preparation and Properties. — Ferrocyanic acid is a white, solid substance, which is readily soluble in water and in alcohol; the solution is sufficiently acid to decompose carbonates and soon becomes blue on exposure to air as a result of decomposition. Oxidation takes place by contact with air, and Prussian blue is formed. The salts of this acid are much more stable than the acid itself, being all prepared from the potassium salt, the so-called *yellow prussiate of potash.* This potassium salt, the most important ferrocyanide of commerce, is obtained by the fusion of organic substances containing nitrogen and sulfur (blood, etc.) with potash and metallic iron, and by lixiviating the product of the fusion with water.

In the melt, iron sulfide and potassium cyanide are found, which, on treatment with water, are changed to potassium ferrocyanide and potassium sulfide,

$$FeS + 6\,KCN \rightarrow K_4[Fe(CN)_6] + K_2S$$

and, on evaporating the solution, the former salt separates out (with three molecules of water of crystallization) in the form of large, yellow, tetragonal octahedrons.

Recently this salt has been obtained as a by-product in the manufacture of illuminating-gas, Prussian blue and ammonium thiocyanate being formed during the purification of the gas.

The following equations will give some idea of the formation of potassium ferrocyanide in the gas-house:

1. $Fe_7(CN)_{18} + 6\,Ca(OH)_2 \rightarrow 4\,\mathbf{Fe(OH)_3} + 3\,\mathbf{Ca_2[Fe(CN)_6]}$
2. $\mathbf{Ca_2[Fe(CN)_6]} + 2\,KCl \rightarrow \underset{\text{Very difficultly soluble}}{\mathbf{K_2Ca[Fe(CN)_6]}} + CaCl_2$
3. $K_2Ca[Fe(CN)_6] + K_2CO_3 \rightarrow \mathbf{CaCO_3} + K_4[Fe(CN)_6]$

Solubility of Ferrocyanides. — The ferrocyanides of the alkalies and alkaline earths are soluble in water; but the remaining salts dissolve with difficulty (if at all) in water and in cold dilute acids. There are many mixed salts, some soluble and some insoluble, *e.g.*, $Ca(NH_4)_2[Fe(CN)_6]$, $Mg(NH_4)_2[Fe(CN)_6]$, and $K_2Sr[Fe(CN)_6]$. The soluble ferrocyanides are yellow when hydrated and colorless when anhydrous.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid.** — The ferrocyanides are not decomposed by cold sulfuric acid, but break up at the boiling temperature with evolution of hydrocyanic acid:

$$2\,K_4[Fe(CN)_6] + 6\,H_2SO_4 \rightarrow K_2Fe[Fe(CN)_6] + 6\,KHSO_4 + 6\,HCN\uparrow$$

2. **Concentrated Sulfuric Acid** decomposes ferrocyanides completely, on warming, with evolution of carbon monoxide, which burns with a blue flame:

$$K_4[Fe(CN)_6] + 11\,H_2SO_4 + 6\,H_2O \rightarrow$$
$$FeSO_4 + 4\,KHSO_4 + 6\,NH_4HSO_4 + 6\,CO\uparrow$$

SO_2 is also liberated by this reaction, for a part of the ferrous sulfate is oxidized by the sulfuric acid to ferric sulfate:

$$2\,FeSO_4 + 2\,SO_3 \rightarrow Fe_2(SO_4)_3 + SO_2\uparrow$$

3. **Silver Nitrate** produces a white precipitate of silver ferrocyanide

$$[Fe(CN)_6]^{=\!=} + 4\,Ag^+ \rightarrow Ag_4[Fe(CN)_6]$$

insoluble in dilute nitric acid and ammonia, but soluble in potassium cyanide solution. On treatment with concentrated nitric acid, it is changed to orange silver ferricyanide, and is then soluble in ammonia.

4. **Barium Chloride** gives no precipitation in dilute solutions. The calcium salt is much less soluble.

5. **Carbon Dioxide.** — Alkali ferrocyanides are *not* decomposed in cold, aqueous solutions by carbon dioxide, but decomposition takes place if carbon dioxide is passed into a hot solution. Solutions of ferrocyanides made alkaline with sodium carbonate give no hydrocyanic acid when distilled in a stream of carbon dioxide; the same is true if sodium bicarbonate is used instead of sodium carbonate in this test.

6. **Cupric** and **Uranyl** salts give brown precipitates, the former in the presence of dilute acetic acid. **Zinc** salts give a white precipitate of $K_2Zn_3[Fe(CN)_6]_2$, insoluble in dilute acids. This precipitate is easily dissolved by caustic alkali;

$$K_2Zn_3[Fe(CN)_6]_2 + 12\,OH^- \rightarrow 2\,[Fe(CN)_6]^{=\!=} + 3\,ZnO_2^{=} + 2\,K^+ + 6\,H_2O$$

By passing CO_2 into the solution, insoluble zinc carbonate is formed.

To detect ferrocyanic acid in an insoluble ferrocyanide, boil the latter with caustic alkali solution; metal hydroxide and a ferrocyanide will be formed. Thus, Prussian blue yields insoluble ferric hydroxide and a soluble ferrocyanide:

$$Fe_4[Fe(CN)_6]_3 + 12\,OH^- \rightarrow 4\,Fe(OH)_3 + 3\,[Fe(CN)_6]^{=\!=}$$

Filter off the insoluble hydroxide, add dilute hydrochloric acid to the filtrate, and treat with ferric chloride. Prussian blue is again formed if a ferrocyanide is present.

Prussian blue is often used in wall-papers as a pigment. If it is desired to detect the presence of this compound in a wall-paper, cut about 100 sq cm of the paper into small pieces, boil them with caustic potash solution, filter, and treat the filtrate according to the method just described. In a few hours a distinct blue precipitate of Prussian blue will be visible in the bottom of the test tube, if it was originally present.

Some insoluble ferrocyanides do not yield the hydroxide of the metal on treatment with caustic alkali. Thus the brown uranyl ferrocyanide yields insoluble yellow potassium uranate and soluble potassium ferrocyanide (cf. Uranium).

The test with normal uranyl acetate solution can be obtained with 1 γ of $K_4Fe(CN)_6$.

7. **Ferric Salts** produce a precipitate of Prussian blue in neutral or acid solutions (cf. p. 215). The test can be obtained with 1γ of $K_4Fe(CN)_6$.

8. **Ferrous Salts** yield a light blue precipitate, which changes to a darker blue on exposure to the air (cf. p. 211).

9. **Hydrochloric Acid.** — If a solution of potassium ferrocyanide, which is not too dilute, is treated with hydrochloric acid, the addition of

ether causes the separation of solid ferricyanic acid at the zone of contact of the ether and aqueous solution.

10. **Lead Salts** precipitate white lead ferrocyanide insoluble in dilute nitric acid.

11. **Thorium Nitrate** added to a slightly acid solution of an alkali ferrocyanide produces a white precipitate, difficult to filter (difference from ferricyanic and thiocyanic acids).

Behavior of Ferrocyanides on Ignition

On being ignited, the ferrocyanides yield iron carbide, cyanide, cyanogen, and nitrogen:

$$3\,K_4[Fe(CN)_6] \rightarrow 12\,KCN + Fe_3C + C + 2\,(CN)_2\uparrow + N_2\uparrow$$

$$3\,Ag_4[Fe(CN)_6] \rightarrow 12\,Ag + Fe_3C + C + 8\,(CN)_2\uparrow + N_2\uparrow$$

FERRICYANIC ACID, $H_3[Fe(CN)_6]$

Anhydrous ferricyanic acid, $H_3[Fe(CN)_6]$, is a non-volatile, brown, crystalline solid readily soluble in water. The solution is brown, and strongly acidic; it is a strong oxidizing agent. Its salts, the ferricyanides, are very stable, and are obtained by *oxidation* of the corresponding ferrocyanides. The most important of all these salts, potassium ferricyanide (red prussiate of potash), $K_3[Fe(CN)_6]$, is obtained by the oxidation of potassium ferrocyanide with chlorine:

$$2\,K_4[Fe(CN)_6] + Cl_2 \rightarrow 2\,KCl + 2\,K_3[Fe(CN)_6]$$

Bromine, hydrogen peroxide, etc., may be used instead of chlorine.

Solubility of Ferricyanides. — The ferricyanides of the alkalies and alkaline earths, and the ferric salt of ferricyanic acid, are soluble in water, but the remaining salts are insoluble even in dilute acids.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** evolves no hydrocyanic acid in the cold (difference from cyanides), but does so on warming with the acid.

2. **Concentrated Sulfuric Acid** decomposes all ferricyanides, on warming, with the formation of sulfates and carbon monoxide:

$$K_3[Fe(CN)_6] + 11\,H_2SO_4 + 6\,H_2O \rightarrow$$
$$FeH(SO_4)_2 + 3\,KHSO_4 + 6\,NH_4HSO_4 + 6\,CO\uparrow$$

3. **Silver Nitrate** produces orange silver ferricyanide:

$$[Fe(CN)_6]^{---} + 3\,Ag^+ \rightarrow \mathbf{Ag_3[Fe(CN)_6]}$$

soluble in ammonia, but insoluble in nitric acid.

4. **Barium Chloride** gives no precipitation.

5. **Behavior of Ferricyanides in Alkaline Solutions.** — Ferricyanic acid is a strong oxidizing agent in alkaline solutions, being readily reduced to ferrocyanic acid by sulfide, iodide, sulfite, ferrous hydroxide, manganous hydroxide, lead oxide, hydrogen peroxide, starch, cellulose (paper), etc.; *e.g.*:

$$2[Fe(CN)_6]^{---} + H_2S^- \rightarrow 2\,[Fe(CN)_6]^{----} + S + 2H^+$$
$$2\,[Fe(CN)_6]^{---} + 2\,I^- \rightarrow 2\,[Fe(CN)_6]^{----} + I_2$$
$$2\,[Fe(CN)_6]^{---} + SO_3^{--} + 2\,OH^- \rightarrow 2\,[Fe(CN)_6]^{----} + SO_4^{--} + H_2O$$
$$2\,[Fe(CN)_6]^{---} + \mathbf{PbO} + 2\,OH^- \rightarrow 2\,[Fe(CN)_6]^{----} + \mathbf{PbO_2} + H_2O$$
$$[Fe(CN)_6]^{---} + \mathbf{Fe(OH)_2} + OH^- \rightarrow [Fe(CN)_6]^{----} + \mathbf{Fe(OH)_3}$$
$$2\,[Fe(CN)_6]^{---} + H_2O_2 + 2\,OH^- \rightarrow 2\,[Fe(CN)_6]^{----} + 2\,H_2O + O_2\uparrow$$

The ferricyanides are even reduced by ammonia, forming nitrogen:

$$6\,[Fe(CN)_6]^{---} + 8\,NH_3 \rightarrow 6\,[Fe(CN)_6]^{--} + N_2\uparrow + 6\,NH_4^+$$

On account of this reducibility of ferricyanic acid, it is often difficult, sometimes impossible, to detect its presence, particularly in an insoluble compound. If Turnbull's blue is boiled with caustic potash, the residue will consist of a mixture of ferrous and ferric hydroxides, and the solution will contain potassium ferrocyanide. See page 211.

6. **Benzidine,** $C_{12}H_{10}(NH_2)_2$, is oxidized by ferricyanic acid with the formation of an insoluble, blue meriquinoidal compound (cf. p. 113). The test is reliable in the absence of other oxidizing agents (chromate, molybdate, etc.).

Place 1 drop of the solution to be tested upon a spot plate and add 1 drop of a cold, saturated solution of benzidine in 2 *N* acetic acid. A blue precipitate or coloration will be obtained with 1 γ of $K_3Fe(CN)_6$. If a ferrocyanide is present, this will form a white precipitate and require more reagent because benzidine ferrocyanide, like benzidine sulfate, is practically insoluble in water. To detect ferricyanide in the presence of considerable ferrocyanide, add 1 drop of 1 per cent lead nitrate solution to the test drop before adding the benzidine acetate reagent. This forms insoluble lead ferrocyanide and prevents interference.

7. **Carbon Dioxide.** — The aqueous solutions of ferricyanides react with carbon dioxide and alkali carbonate in the same manner as ferrocyanides (p. 334).

8. **Cupric Salts** yield green cupric ferricyanide:

$$2\,[Fe(CN)_6]^{---} + 3\,Cu^{++} \rightarrow Cu_3[Fe(CN)_6]_2$$

9. **Ferric Salts** produce no precipitation, but a brown coloration.

10. **Ferrous Salts** produce, in neutral and acid solutions, a precipitate of Turnbull's blue (cf. p. 211).

11. **Hydrogen Sulfide** reduces alkali ferricyanide to alkali ferrocyanide:

$$2\,[Fe(CN)_6]^{---} + H_2S \rightarrow 2\,[Fe(CN)_6]^{--} + 2\,H^+ + S$$

12. **Manganous Chloride** in concentrated hydrochloric acid is darkened by ferricyanic acid. This test merely shows that an oxidizer is present.

13. **Mercuric Oxide.**—The behavior of cyanides toward suspended, yellow mercuric oxide is very important. Almost all cyanides, simple or complex, with the exception of potassium cobalticyanide, are completely decomposed by this reagent. Mercuric cyanide and an oxide of the other metal are formed, and the latter, if insoluble, may be separated from the mercuric cyanide by filtration. Thus potassium ferrocyanide is decomposed by mercuric oxide as follows:

$$K_4[Fe(CN)_6] + 3\,HgO + 3\,H_2O \rightarrow Fe(OH)_3 + 4\,KOH + 3\,Hg(CN)_2$$

Prussian blue as follows:

$$Fe_4[Fe(CN)_6]_3 + 9\,HgO + 9\,H_2O \rightarrow 3\,Fe(OH)_2 + 4\,Fe(OH)_3 + 9\,Hg(CN)_2$$

This decomposition of the cyanides by mercuric oxide is often used in quantitative analysis for the separation of metallic cyanides.

Behavior of Ferricyanides on Ignition

The ferricyanides are decomposed into iron carbide, cyanide, cyanogen, carbon, and nitrogen:

$$6\,K_3[Fe(CN)_6] \rightarrow 18\,KCN + 2\,Fe_3C + 10\,C + 3\,(CN)_2 + 6\,N_2$$

By heating a ferricyanide in a closed tube, cyanogen is given off, which burns with a reddish flame.

THIOCYANIC ACID, HCNS

Thiocyanic acid is found in small amounts, in the form of its sodium salt, in saliva and urine.

The free acid is a colorless, unstable liquid, with a penetrating odor. It freezes at 5° and boils at 85°. It is soluble in water and in alcohol. The aqueous solutions are about as strongly acidic as hydrochloric acid, the ionization being nearly complete in dilute solutions. It can be kept better in aqueous solution than in the anhydrous state, but its salts, the thiocyanates, are much more stable than the acid itself. The products formed by the decomposition of a concentrated solution of thiocyanic acid are hydrocyanic acid, HCN, and yellow perthiocyanic acid, $H_2(CNS)_2S$. The alkali salts of thiocyanic acid can be prepared from the corresponding cyanides by heating with sulfur:

$$KCN + S \rightarrow KCNS$$

They may also be prepared by treating hydrocyanic acid or an alkali cyanide with an alkali polysulfide at ordinary temperatures,

$$KCN + (NH_4)_2S_2 \rightarrow (NH_4)_2S + KCNS$$

or by boiling an alkali thiosulfate solution with an alkali cyanide (cf. p. 414):

$$Na_2S_2O_3 + KCN \rightarrow Na_2SO_3 + KCNS$$

The easiest way to prepare ammonium thiocyanate is to allow a mixture of 30 ml concentrated ammonium hydroxide, 30 ml of alcohol, and 7 ml of carbon disulfide to evaporate very slowly on the water-bath. First of all, ammonium thiocarbamate is formed,

$$CS_2 + 2\ NH_3 \rightarrow NH_4CS_2NH_2$$

and during the evaporation this loses hydrogen sulfide:

$$NH_4CS_2NH_2 \rightarrow NH_4CNS + H_2S\uparrow$$

Solubility. — Most thiocyanates are soluble in water; exceptions are the silver, mercury, copper, and gold salts. Lead thiocyanate is difficultly soluble in water; on boiling with water it is decomposed.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** (double normal) causes no reaction.

2. **Moderately Concentrated Sulfuric Acid** (14-normal) decomposes the thiocyanates, with evolution of carbonyl sulfide, which burns with a blue flame:

$$KCNS + 2\ H_2SO_4 + H_2O \rightarrow KHSO_4 + (NH_4)HSO_4 + COS\ \uparrow$$

3. **Concentrated Sulfuric Acid** violently decomposes thiocyanates with evolution of very disagreeably smelling vapors (COS, HCOOH, CO_2, SO_2), and deposition of sulfur.

4. **Silver Nitrate** precipitates white, curdy, silver thiocyanate,

$$CNS^- + Ag^+ \rightarrow \mathbf{AgCNS}$$

insoluble in dilute nitric acid, soluble in ammonia.

5. **Cobalt Salts.** — If a solution containing an alkali thiocyanate is treated with a small amount of a cobalt salt, and the solution shaken with a mixture of equal parts amyl alcohol and ether, the upper layer of alcohol and ether separates out azure-blue in color (cf. p. 240). This reaction is analogous to that of cyanic acid upon cobalt salts (cf. p. 360).

6. **Cupric Salts.** — On adding a few drops of a solution containing a cupric salt to one of an alkali thiocyanate, the solution is colored emerald-green; and, on further addition of the copper solution, black cupric thiocyanate is precipitated. If sulfurous acid is added, white cuprous thiocyanate is deposited,

$$2\ Cu^{++} + SO_3^{--} + 2\ CNS^- + H_2O \rightarrow \mathbf{Cu_2(CNS)_2} + 2\ H^+ + SO_4^{--}$$

insoluble in dilute hydrochloric and sulfuric acids.

7. **Ferric Salts** produce a blood-red coloration, due to the formation of non-ionized ferric thiocyanate,

$$3\ CNS^- + Fe^{+++} \rightarrow Fe(CNS)_3$$

very soluble in ether (cf. p. 215).

The test cannot be obtained satisfactorily in the presence of oxalic acid, tartaric acid, other hydroxyorganic acids, phosphoric acid, ferrocyanic acid, and iodides. All these, except the last, form complexes with Fe^{+++} and prevent the formation of $Fe(CNS)_3$. Iodides interfere because the iodide ion is oxidized to free iodine by ferric ions and the aqueous solution of iodine is red.

8. **Mercuric Chloride** gives a precipitate only after long standing.

9. **Mercuric Nitrate** precipitates white mercuric thiocyanate,

$$Hg^{++} + 2\ CNS^- \rightarrow \mathbf{Hg(CNS)_2}$$

very difficultly soluble in water, but readily soluble in an excess of potassium thiocyanate:

$$\mathbf{Hg(CNS)_2} + CNS^- \rightarrow [Hg(CNS)_3]^-$$

If dry $K[Hg(CNS)_3]$ is heated, the salt expands greatly (Pharaoh's serpents).

10. **Mercurous Nitrate.** — On adding mercurous nitrate drop by drop to a fairly concentrated solution of potassium thiocyanate, a gray precipitate of metallic mercury is first obtained, and the solution contains potassium mercuric thiocyanate:

$$\mathbf{Hg_2^{++}} + 3\ CNS^- \rightarrow [Hg(CNS)_3]^- + \mathbf{Hg}$$

If the addition of mercurous nitrate is continued until no more mercury is precipitated, and the solution then filtered, the filtrate will contain potassium mercuric thiocyanate; but, on adding still more mercurous nitrate, pure white mercurous thiocyanate is precipitated:

$$2\,[Hg(CNS)_3]^- + 3\,Hg_2^{++} \rightarrow 2\,Hg^{++} + \mathbf{3\,Hg_2(CNS)_2}$$

If, on the other hand, a very dilute solution of potassium thiocyanate is added to a very dilute solution of mercurous nitrate, the white precipitate of mercurous thiocyanate is obtained directly:

$$Hg_2^{++} + 2\,CNS^- \rightarrow \mathbf{Hg_2(CNS)_2}$$

11. **Nitric Acid,** even when dilute, causes decomposition and the formation of nitric oxide, carbon dioxide, and sulfuric acid:

$$3\,CNS^- + 10\,H^+ + 13\,NO_3^- \rightarrow 16\,NO\uparrow + 3\,CO_2\uparrow + 3\,SO_4^{--} + 5\,H_2O$$

12. **Sodium Azide,** NaN_3, and **Iodine** react in the presence of soluble and insoluble thiocyanates with liberation of nitrogen gas.

The reaction $2\,NaN_3 + I_2 \rightarrow 2\,NaI + 3\,N_2\uparrow$ takes place extremely slowly, if at all, in the absence of a catalyst.

Mix on a spot plate 1 drop of the solution to be tested with 1 drop of a solution obtained by dissolving 3 g of sodium azide in 100 ml of 0.1 *N* iodine solution. The evolution of nitrogen is perceptible if 1.5 γ of KCNS is present.

This test is valuable because, unlike the ferric chloride test, it can be carried out in the presence of iodide. Iodide, however, retards the reaction, and when much is present a drop of mercuric chloride should be added before adding the sodium azide reagent; thereby the $[HgI_4]^{--}$ complex is formed. Sulfides and thiosulfates also catalyze the reaction between sodium azide and iodine; they can be removed by precipitation with mercuric chloride and filtering off the precipitate of mercuric sulfide.

13. **Zinc** added to an acid solution of a thiocyanate causes the formation of hydrogen cyanide and hydrogen sulfide:

$$\mathbf{Zn} + SCN^- + 3\,H^+ \rightarrow Zn^{++} + H_2S\uparrow + HCN\uparrow$$

SPECIAL PROCEDURES FOR THIOCYANATE

Detection of Thiocyanates in the Presence of Halides and Cyanide

First free the solution from hydrocyanic acid by adding a little sodium bicarbonate, heating to boiling, and passing carbon dioxide gas through the solution until the escaping gas led into slightly acid silver nitrate solution gives no turbidity of silver cyanide.

After the removal of the hydrocyanic acid, test for thiocyanate, *in the absence of iodide*, by acidifying with hydrochloric acid and adding a few drops of ferric chloride. *A blood-red coloration shows the presence of thiocyanate.* The test cannot be obtained satisfactorily in the presence of an iodide because it also will react with ferric chloride, causing liberation of free iodine.

If an iodide is present, add a little nitric acid to the solution from which the hydrocyanic acid has been expelled, and precipitate the halogens and thiocyanate by the addition of an excess of silver nitrate solution. After the precipitate has settled, decant off the supernatant solution and wash the precipitate several times by decantation with water. Then shake the precipitate vigorously with 6-normal ammonia solution. This dissolves the chloride and thiocyanate readily, all or a part of the bromide, but no appreciable quantity of silver iodide. Filter and add colorless ammonium sulfide to the filtrate. Filter off the silver sulfide precipitate, add a drop of sodium carbonate solution, evaporate to small volume, acidify with hydrochloric acid, and test for thiocyanate with ferric chloride solution.

Detection of Halogens in the Presence of Thiocyanate

VOLHARD'S METHOD

Treat the nitric acid solution with an excess of silver solution, filter, and dry the precipitate with suction. Transfer the precipitate to a porcelain dish and heat it on the water-bath for 45 minutes with concentrated nitric acid. This causes the complete decomposition of all the thiocyanate,

$$6\,AgCNS + 4\,H_2O + 16\,HNO_3 \rightarrow 3\,Ag_2SO_4 + 3\,(NH_4)_2SO_4 + 6\,CO_2\uparrow + 16\,NO\uparrow$$

but the silver halides are not attacked appreciably. Dilute, filter, and wash a few times with hot water. Reduce the precipitate with zinc and dilute sulfuric acid (p. 104), filter, and test this filtrate according to page 321.

Or, instead of treating the washed silver precipitate with nitric acid, it may be boiled with sulfuric acid (1 : 1) until the precipitate becomes black and collects in a ball:

$$2\,AgCNS + 2\,H_2SO_4 + 3\,H_2O \rightarrow 2\,NH_4HSO_4 + COS\uparrow + CO_2\uparrow + Ag_2S$$

Dilute the solution with water, filter off the silver halides and silver sulfide, wash with water, reduce with zinc and sulfuric acid, and test for the halogens after boiling off the hydrogen sulfide from the last filtrate.

Remark. — It is always necessary to destroy the thiocyanate before reducing with zinc and sulfuric acid, because otherwise hydrocyanic acid will be formed:

$$2\,AgSCN + 3\,Zn + 6\,H^+ \rightarrow 2\,Ag + 3\,Zn^{++} + 2\,HCN\uparrow + 2\,H_2S\uparrow$$

According to A. W. Hofmann, *free* thiocyanic acid on being reduced with zinc and acid yields a mixture of thioformaldehyde, methylamine, ammonium salt, and hydrogen sulfide.

Testing Commercial Alkali Thiocyanate for Chloride

MANN'S METHOD

Dissolve 5 g of the alkali thiocyanate in 20 ml of water and to the solution add 20 g of crystallized copper sulfate dissolved in 100 ml of water. A black precipitate of cupric thiocyanate is formed:

$$Cu^{++} + 2\,CNS^- \rightarrow Cu(CNS)_2$$

Pass hydrogen sulfide gas through the solution until the precipitate becomes nearly white:

$$2\,Cu(CNS)_2 + H_2S \rightarrow Cu_2(CNS)_2 + S + 2\,HCNS$$

Then, when the supernatant blue copper solution begins to get brown, owing to the formation of copper sulfide, stop introducing the hydrogen sulfide gas and al-

low the liquid to stand a few hours. During this time the thiocyanic acid formed by the above reaction is acted upon by the copper sulfide present, as follows:

$$2\ Cu(CNS)_2 + 2\ CuS \rightarrow 2\ Cu_2(CNS)_2 + 2\ S$$

Filter and treat the filtrate with silver nitrate. A white precipitate shows chloride to be present.

Remark. — An equally good method is the following: Treat the solution of the thiocyanate with an excess of copper sulfate solution and introduce sulfur dioxide gas until the precipitate becomes white cuprous thiocyanate. Allow the solution to stand several hours, then filter off the cuprous thiocyanate, treat the filtrate with nitric acid, and test for chlorine with silver nitrate.

Instead of sulfurous acid, hydroxylamine sulfate may be used to reduce the cupric solution.

Detection of Ferro- and Ferricyanides in the Presence of Thiocyanate

Method of P. E. Browning and H. E. Palmer

Acidify the dilute solution of the alkali salts of these acids with acetic acid or hydrochloric acid, avoiding an excess, and add a solution of thorium nitrate; finely divided thorium ferrocyanide will be precipitated. Shake the solution with finely divided asbestos, or filter paper pulp, filter, and wash the precipitate with cold water. Pour dilute sodium hydroxide solution over the precipitate, acidify the solution thus obtained, and add a few drops of ferric chloride; *Prussian blue is formed if a ferrocyanide was present.*

Add cadmium sulfate solution to the filtrate from the thorium ferrocyanide precipitate, shake with finely divided asbestos, and filter off the cadmium ferricyanide. Wash the precipitate with cold water, dissolve in sodium hydroxide solution, acidify the solution with hydrochloric acid, and treat with ferrous sulfate solution. *The formation of Turnbull's blue shows the presence of ferricyanic acid.*

Add ferric chloride to the filtrate from the cadmium ferricyanide precipitate; *a blood-red coloration will be obtained if a thiocyanate is present.*

Behavior of Thiocyanates on Ignition

The thiocyanates of the alkalies melt readily, and are colored successively yellow, brown, green, and finally blue, becoming white again on cooling.

The thiocyanates of the heavy metals are decomposed into sulfide, splitting off carbon disulfide, cyanogen, and nitrogen. Thus cuprous thiocyanate is decomposed according to the following equation:

$$4\ Cu_2(CNS)_2 \rightarrow 4\ Cu_2S + 2\ CS_2\uparrow + 3\ (CN)_2\uparrow + N_2\uparrow$$

The mercuric thiocyanates swell tremendously on being heated (Pharaoh's serpents).

COBALTICYANIC ACID, $H_3[Co(CN)_6]$

Preparation. — The free acid can be obtained by suspending the lead or copper salt in water and saturating the water with hydrogen sulfide gas; the lead or copper cobalticyanide is changed into less soluble sulfide and, by filtering, an aqueous solution of cobalticyanic acid is obtained from which the solid acid deposits upon evaporation. The free acid may be prepared also by treating the potassium salt with nitric acid, evaporating to dryness on the water-bath, and extracting the acid with alcohol. After evaporating off the alcohol, needle-shaped hygroscopic crystals of $H_3[Co(CN)_6]$ are obtained.

Properties. — Cobalticyanic acid is extremely stable. It is not decomposed by boiling with concentrated hydrochloric or nitric acid, by chlorine, or by boiling with HgO. By heating with concentrated sulfuric acid, however, it is decomposed with evolution of carbon monoxide and carbon dioxide:

$$2\,H_3[Co(CN)_6] + 8\,H_2SO_4 + 13\,H_2O \rightarrow 2\,CoSO_4 + 6\,(NH_4)_2SO_4 + 11\,CO\uparrow + CO_2\uparrow$$

Solubility of Cobalticyanides. — The alkali, alkaline earth, ferric, and other trivalent metal salts are soluble in water. Most of the other salts with bivalent metals and with heavy metals are insoluble in water and in acids.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid.** No reaction.
2. **Concentrated Sulfuric Acid** decomposes all the salts with evolution of CO and CO_2 and formation of blue, anhydrous cobaltous salt.
3. **Silver Nitrate** produces a white precipitate insoluble in nitric acid but soluble in ammonia.
4. **Cadmium Sulfate** and **Zinc Sulfate** give white precipitates insoluble in nitric acid but soluble in ammonia.
5. **Cobaltous Nitrate** produces a pink precipitate insoluble in nitric acid but soluble in ammonia.
6. **Copper Sulfate** produces a light blue precipitate insoluble in nitric acid but forming a blue solution with ammonia.
7. **Ferrous Sulfate** produces a white precipitate insoluble in nitric acid.
8. **Lead Acetate, Ferric Chloride,** and **Mercuric Chloride** produce no precipitates.
9. **Nickel Sulfate** gives a blue precipitate insoluble in nitric acid but soluble in ammonia.
10. **Mercuric Nitrate** produces a white, voluminous precipitate insoluble in nitric acid.

Reactions in the Dry Way

All the salts of cobalticyanic acid are decomposed by ignition, leaving cyanide and cobalt carbide behind. The alkali and alkaline earth salts color the borax bead blue in both the oxidizing and reducing flames.

GROUP II

Silver Nitrate produces a precipitate soluble in nitric acid.
Barium Chloride causes no precipitation.

NITROUS ACID, HNO_2

Occurrence. — Nitrous acid never occurs except in the form of its salts, the nitrites. It is found in the air as ammonium nitrite and in many soils and waters, particularly in those which are contaminated with ammonia or decaying substances.

Ammonia is oxidized by the action of microörganisms (*Monas nitrificans*) to nitrous acid, which combines with more ammonia to form ammonium nitrite.

Preparation and Properties of Nitrous Acid and Its Salts. — Nitrous acid is formed by the gentle reduction of nitric acid. If zinc is allowed to act upon dilute nitric acid for a short time, the latter is reduced to nitrous acid,

$$Zn + 3\ HNO_3 \rightarrow Zn(NO_3)_2 + HNO_2 + H_2O,$$

but the reduction can easily go a little farther, forming NO, N_2O, and N_2; while by long-continued action of the zinc, hydroxylamine, NH_2OH, or even ammonia is formed.

If nitric acid of density 1.3 is heated with arsenious acid, starch, etc., a mixture of nitric oxide and nitrogen dioxide is obtained, which, on cooling to $-21°$ C, condenses to a bluish green liquid, N_2O_3, the anhydride of nitrous acid. If the anhydride is treated with ice-cold water, a bluish green liquid is obtained, which contains nitrous acid, but always in company with nitric acid; for N_2O_3 unites with water, forming nitrous and nitric acids, and nitric oxide:

$$2\ N_2O_3 + H_2O \rightarrow HNO_3 + HNO_2 + 2\ NO$$

At a higher temperature nitrous acid is gradually changed into nitric acid:

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$$

Pure nitrous acid, therefore, is not known. In aqueous solution it exists as a fairly strong acid, the ionization constant being 0.45×10^{-3}; it is ionized about twenty times as much as acetic acid in 0.1-normal solution.

If a mixture of nitric oxide and nitrogen dioxide is conducted into concentrated sulfuric acid, the two gases are readily absorbed, forming nitrosylsulfuric acid:

$$2\ H_2SO_4 + NO + NO_2 \rightarrow H_2O + 2\ H(NO)SO_4$$

This solution of nitrosylsulfuric acid in sulfuric acid is sometimes called "nitrose." If the solution is added to cold water, sulfuric and nitrous acids are formed:

$$H(NO)SO_4 + H_2O \rightarrow HNO_2 + H_2SO_4$$

A solution of nitrosylsulfuric acid can be kept indefinitely, so that it is a convenient reagent for the immediate production of nitrous acid at any time.

The salts of nitrous acid, the nitrites, are much more stable than the free acid, and may be obtained by the ignition of nitrates:

$$2\ NaNO_3 \rightarrow 2\ NaNO_2 + O_2$$

Nitrites prepared in this way always contain some oxide and some nitrate as impurity.* In order to obtain a pure nitrite, silver nitrite is treated with the calculated amount of a metallic chloride:

$$AgNO_2 + NaCl \rightarrow AgCl + NaNO_2$$

The soluble nitrite can be separated from the insoluble silver chloride by filtration.

Solubility of Nitrites. — All nitrites are soluble in water; silver nitrite is difficultly soluble.

Reactions in the Wet Way

Since all nitrites are soluble in water, the reactions which serve for the detection of this acid cannot be those of precipitation, but rather those in which a change of color takes place, owing to an oxidation or reduction.

Nitrous acid sometimes acts as an oxidizing agent, and sometimes as a reducing agent.

1. **Dilute Sulfuric Acid** decomposes all nitrites in the cold, setting free brown vapors:

$$NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HNO_2$$
$$3\,HNO_2 \rightarrow HNO_3 + 2\,NO\uparrow + H_2O$$
$$2\,NO + O_2\,(\text{air}) \rightarrow 2\,NO_2\uparrow$$

2. **Concentrated Sulfuric Acid** reacts exactly the same, but much more violently.

3. **Silver Nitrate** precipitates from nitrite solutions crystals of silver nitrite in the form of needles, which are slightly soluble in cold water (300 ml of water dissolves 1 g of silver nitrite at room temperature). In boiling water, silver nitrite is considerably more soluble.

4. **Aluminum** in the presence of sodium hydroxide reduces nitrite solutions to ammonia. A similar reaction takes place with nitrates:

$$NO_2^- + 2\,Al + OH^- + H_2O \rightarrow 2\,AlO_2^- + NH_3\uparrow$$

5. **Ammonium chloride,** on being added to a boiling solution of a nitrite in dilute acetic acid, causes evolution of nitrogen gas:

$$NH_4^+ + NO_2^- \rightarrow 2\,H_2O + N_2\uparrow$$

6. **Brucine** dissolved in concentrated sulfuric acid (according to G. Lunge and A. Lwoff†) gives no reddish coloration when treated with nitrosylsulfuric acid.

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* If the nitrate is heated with a metal, *e.g.*, lead, the reduction takes place at a lower temperature and is almost quantitative.

† *Z. angew. Chem.*, **1894**, 345.

Dry, recrystallized silver nitrite, containing 70.05 per cent silver (theory 70.09), did give with brucine (cf. p. 417), in an atmosphere of carbon dioxide, a weak but nevertheless distinct test for nitric acid, probably because of the presence of traces of nitrate remaining in the silver nitrite. On dissolving 15 mg of this same nitrite in water, adding an equivalent amount of sodium chloride, and diluting to 1 l, a solution of sodium nitrite was obtained, of which 1 ml added *drop by drop* with *constant stirring* to about 4 ml of concentrated sulfuric acid yielded a solution of nitrosylsulfuric acid which gave no sign of a red coloration with a drop of brucine reagent. The test was immediately obtained, however, on adding a trace of nitric acid to this solution.

Brucine, therefore, is a reagent by which nitric acid can be detected in the presence of nitrous acid.

7. **Cobalt Salts** produce (with an excess of potassium nitrite and acetic acid) a yellow crystalline precipitate of potassium cobaltinitrite (cf. p. 244).

8. **Diphenylamine,** dissolved in concentrated sulfuric acid, is colored intensely blue by nitrous acid. Nitric acid and many other oxidizing substances, such as selenic acid, chloric acid, ferric chloride, etc., will give the same reaction (cf. Nitric Acid).

9. **Ferrous Salts** are oxidized to ferric salts, with evolution of nitric oxide:

$$Fe^{++} + NO_2^- + 2\,H^+ \rightarrow Fe^{+++} + NO\uparrow + H_2O$$

The nitric oxide dissolves, in the cold, in the excess of ferrous salt, forming a brown compound of a varying composition: $(FeSO_4)_x(NO)_y$.

To obtain this compound, add a little acid to a concentrated solution of ferrous sulfate and carefully pour the solution to be tested on top. At the zone of contact between the two solutions the dark brown coloration will be apparent.

Nitric acid gives the same reaction, but only on the addition of concentrated sulfuric acid. Citric or acetic acid furnishes sufficient H^+ ions to give the test with a nitrite.

10. **Detection of Small Amounts of Nitrous Acid by the Peter Griess Method.*** — To detect the small amounts of nitrous acid which may be present in drinking water, of the above reactions only that of potassium iodide and starch is delicate enough. But since hydrogen peroxide and ferric salts are also likely to be present, both of which cause the separation of iodine from an acid solution of potassium iodide, it is evident that dependence upon this reaction alone would often lead to error.

Consequently, in order to detect the presence of traces of nitrous acid we make use of a reaction which was first proposed by Peter Griess, and which is caused by nitrous acid only. It depends upon the formation of an intensely colored azo-dyestuff.

Peter Griess used as his reagent phenylenediamine, whereby a yellow dye, Bis-

* *Ber.*, **12**, 427 (1879).

marck brown, is formed. According to the suggestion of Ilosvay v. Ilosva,* an acetic acid solution of sulfanilic acid and of α-naphthylamine is used instead. According to Lunge,† it is best to mix the solutions of the last two reagents.

The reagent is prepared as follows:

(*a*) Dissolve 0.5 g of sulfanilic acid in 150 ml of 2-normal acetic acid.

(*b*) Boil 0.2 g of solid α-naphthylamine with 20 ml of water, pour off the colorless solution from the bluish violet residue, and add to the colorless solution 150 ml of 2-normal acetic acid.

Mix the two solutions. The mixture keeps well only when kept in a dark place. It turns reddish if exposed to the light, and cannot be decolorized by shaking with zinc.

Procedure. — Treat about 50 ml of the water with 2 ml of the above reagent, and allow it to stand five or ten minutes; it will be colored a distinct red if a trace of nitrous acid is present.

11. **Hydriodic Acid** is oxidized by nitrous acid with separation of iodine:

$$2\,I^- + 2\,NO_2^- + 4\,H^+ \rightarrow 2\,H_2O + 2\,NO\uparrow + I_2$$

If, therefore, a nitrite is added to a solution of potassium iodide and the solution is acidified with sulfuric or acetic acid, the solution becomes yellow, owing to the separation of iodine. If the solution is now shaken with chloroform or carbon disulfide, the latter will be colored reddish violet. Or, if a little starch paste is added, it will be colored blue by the iodine.

As the above equation shows, hydrogen ions are required in the reaction. If considerable alkali acetate is present, there is no separation of iodine on the addition of acetic acid, but if a few drops of a strong mineral acid are added, iodine is at once set free. This is a good illustration of the mass-action principle (p. 2) and common-ion effect (p. 49).

This exceedingly delicate reaction is also caused by the action of a great many other oxidizing agents; and it can be used for the detection of nitrous acid only when it is known that all such oxidizing substances are absent.

Since ferric salts also cause liberation of iodine (cf. p. 39) it is evident that nitrous acid cannot be tested for by the above test in the presence of a ferric salt. If, however, a large excess of sodium phosphate is added to the solution, together with a little potassium iodide and some sulfuric acid, no iodine will be liberated by the ferric salt and the presence of a trace of nitrous acid may be detected. The ferric ions are converted into very slightly ionized ferric acid phosphate in this test, and the concentration of the ferric ions is made so small that there is no appreciable reaction with the iodide ions. Artmann,‡ who suggested this procedure, adds 8 g $Na_2HPO_4 \cdot 12\,H_2O$, 0.2 g KI, 5 ml 4-normal H_2SO_4, and a little starch solution to 100 ml of a solution of the ferric salt which is to be tested for nitrite. If as much as 0.3 mg of N_2O_3 is present, the intense blue color will be obtained immediately.

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* *Bull. chim.* [3] **2**, 317.

† *Z. angew. Chemie*, **1889**, Heft 23.

‡ *Chem., Ztg.*, **1913**, 501.

12. **Hydrogen Sulfide** gives a precipitate of sulfur. This forms immediately in acid solutions and very slowly in neutral solutions:

$$2\,NO_2^- + H_2S + 2\,H^+ \rightarrow 2\,NO\uparrow + 2\,H_2O + S$$

13. **Indigo Solution** is completely decolorized by warming with nitrous acid.

14. **Manganous Chloride** in concentrated hydrochloric acid is darkened by nitrous acid. This test merely shows that an oxidizer is present.

15. **Potassium Permanganate.** — If nitrous acid is added to a warm (about 40° C) acid solution of potassium permanganate, the latter will become decolorized, owing to the oxidation of the former to nitric acid:

$$2\,MnO_4^- + 5\,NO_2^- + 6\,H^+ \rightarrow 2\,Mn^{++} + 5\,NO_3^- + 3\,H_2O$$

In this reaction nitrous acid acts as a reducing agent.

16. **Potassium Thiocyanate** does not react with a neutral or slightly acid solution of a nitrite. On adding a strong mineral acid, however, a dark red color is obtained. This color is similar to that produced by a ferric salt and thiocyanate and is due to an oxidation of the thiocyanate. The addition of alcohol, or gently boiling, destroys the color produced by nitrous acid; shaking with carbon disulfide removes the greater part of the color.

17. **Resorcinol,** $C_6H_4(OH)_2$, is useful for the detection of small quantities of nitrous acid dissolved in concentrated sulfuric acid. The test is made as follows:

Take 1 ml of the concentrated sulfuric acid, add just a trace of resorcinol, and dilute with 5 ml of water. A mere trace of nitrous acid gives a yellow color.

18. **Thiourea,** $CS(NH_2)_2$, reacts with nitrous acid to form nitrogen gas and thiocyanic acid:

$$HNO_2 + CS(NH_2)_2 \rightarrow N_2\uparrow + HCNS + 2\,H_2O$$

This reaction takes place best in very dilute acetic acid solutions containing sodium acetate. The presence of nitrite is indicated by the formation of the gas and by the red color which the resulting thiocyanic acid gives with ferric ions.

19. **Urea** acts with nitrous acid with evolution of nitrogen and carbon dioxide:

$$CO(NH_2)_2 + 2\,HNO_2 \rightarrow 3\,H_2O + CO_2\uparrow + 2\,N_2\uparrow$$

In this reaction the nitrogen of the urea, with its negative valence of three, is oxidized by the nitrogen of nitrous acid, which has a positive valence of three. In alkaline solutions free halogens will react with urea, but in acid solutions the reaction with nitrous acid is sensitive and characteristic.

HYDROGEN SULFIDE (HYDROSULFURIC ACID), H_2S

Occurrence and Preparation. — Hydrogen sulfide is found in volcanic regions, in many mineral waters (the so-called "sulfur" waters), and, in general, wherever substances containing sulfur are subject to decay, or when they come in contact with decaying substances. Sulfates are easily changed into sulfides by the action of microörganisms which are present in the air; this is the reason why many mineral waters containing sulfates smell of hydrogen sulfide after standing some time in a corked flask. If, however, the flask and the cork are sterilized, the water can be kept indefinitely. The formation of hydrogen sulfide from sulfates takes place as follows:

By means of carbonaceous matter (dust, etc.) the sulfate is reduced with the aid of microörganisms, at first to sulfide,

$$Na_2SO_4 + 2\,C \rightarrow 2\,CO_2 + Na_2S$$

which is then decomposed by carbonic acid:

$$Na_2S + H_2CO_3 \rightarrow Na_2CO_3 + H_2S\uparrow$$

Just as hydrogen sulfide may be made from sodium sulfate by the action of organic matter in a corked flask, so in nature the same process brings about the presence of hydrogen sulfide in many mineral waters.

For laboratory purposes, hydrogen sulfide is prepared by the action of dilute sulfuric or hydrochloric acid upon a sulfide, usually iron sulfide, FeS, on account of its cheapness and stability; pyrite, FeS_2, does *not* react with dilute mineral acids.

Properties. — Hydrogen sulfide is a colorless gas, with an odor like that of rotten eggs; it is absorbed by water at ordinary temperatures (one volume of water absorbs two to three times its own volume). The saturated solution at 25° is approximately 0.1 molar = 0.2 normal. The higher the temperature, the less the solubility, as with all gases. For the primary ionization: $H_2S \rightleftarrows H^+ + HS^-$, the value of the ionization constant

$$\frac{[H^+] \times [HS^-]}{[H_2S]} = k_1 \text{ is } 0.91 \times 10^{-7}$$

For the secondary ionization, $HS^- \rightarrow H^+ + S^{--}$, the value of the constant

$$\frac{[H^+] \times [S^{--}]}{[HS^-]} = k_2 \text{ is } 1.2 \times 10^{-15}$$

In the saturated solution at 25°, the concentration of the hydrogen ion is about 0.9×10^{-4} mole per liter and of the simple sulfide ion is only 1.2×10^{-15}. According to the table on page 62, therefore, a saturated solution of hydrogen sulfide should react acid to phenolphthalein but not to methyl orange.

The solution of hydrogen sulfide becomes turbid on standing in the air as a result of its oxidation by atmospheric oxygen:

$$2\,H_2S + O_2 \rightarrow 2\,H_2O + 2\,S$$

Hydrogen sulfide burns in the air with a bluish flame to water and sulfur dioxide:

$$2\,H_2S + 3\,O_2 \rightarrow 2\,H_2O + 2\,SO_2$$

The gas can be condensed to a solid which melts at −83° and the liquid boils at −60.2°.

The salts of hydrosulfuric acid are called sulfides.

Solubility of Sulfides.—The sulfides of the alkalies and the hydro- and polysulfides of the alkaline earths are soluble in water. The monosulfides of the alkaline earths, particularly calcium sulfide, CaS, are difficultly soluble in water, but they are gradually changed by contact with water into soluble hydrosulfides:

$$2\,CaS + 2\,H_2O \rightarrow Ca(OH)_2 + Ca(SH)_2$$

The remaining sulfides are insoluble in water. Of these latter FeS, MnS, and ZnS are decomposed by dilute hydrochloric acid with evolution of hydrogen sulfide; others require concentrated hydrochloric acid, *e.g.*, Sb_2S_3, SnS_2, PbS, NiS, CoS, CdS; the remaining are insoluble in concentrated hydrochloric acid, but are all soluble in aqua regia with separation of sulfur.

Reactions in the Wet Way

Free hydrogen sulfide, as has been stated, is a very weak acid, being even weaker than carbonic acid. The soluble neutral salts, R_2S, on being dissolved, ionize into metal and sulfide ions,

$$R_2S \rightleftarrows 2\,R^+ + S^{--}$$

but under the influence of water, some of the bivalent sulfur ions are changed to univalent HS^- ions,

$$HOH + S^{--} \rightleftarrows HS^- + OH^-$$

some of the bivalent sulfides ions remain in solution, and, in fact, more in concentrated solutions than in dilute ones.

Since, therefore, an aqueous solution of a sulfide contains both S^{--} ions and SH^- ions, while the solutions of the free acid contain chiefly non-ionized H_2S, it is plain why in many reactions the former react in a somewhat different way from the latter.

1. **Dilute Sulfuric Acid** decomposes all soluble, and some insoluble, sulfides, with evolution of hydrogen sulfide.

2. **Concentrated Sulfuric Acid** decomposes all sulfides, on warming, with evolution of sulfur dioxide and deposition of sulfur:

$$Na_2S + 2\,H_2SO_4 \rightarrow Na_2SO_4 + 2\,H_2O + SO_2\uparrow + S$$

But even the sulfur goes over into sulfur dioxide after being heated with the sulfuric acid for some time:

$$2\,H_2SO_4 + S \rightarrow 2\,H_2O + 3\,SO_2\uparrow$$

3. **Silver Nitrate** produces, in solutions of hydrogen sulfide and of soluble sulfides, a black precipitate of silver sulfide,

$$2\,Ag^+ + H_2S \rightarrow Ag_2S + 2\,H^+$$

insoluble in cold nitric acid, in which, however, it dissolves on warming (cf. p. 102).

4. **Barium Chloride** causes no precipitation.

5. **Lead Salts** (best a solution containing an excess of alkali) produce a black precipitate of lead sulfide. All sulfides which are decomposed by hydrochloric acid evolve hydrogen sulfide, and this gas, on coming in contact with a piece of filter paper moistened with an alkaline lead solution, colors the latter black. An insoluble sulfide (pyrite, arsenic sulfide, mercuric sulfide, etc.) evolves hydrogen sulfide when treated with hydrochloric acid and tin or zinc.

To test an insoluble sulfide, such as the mineral pyrite, place a little finely granulated tin in a test tube, cover it with 6-normal hydrochloric acid, and heat gently. Hold a piece of filter paper which has been moistened with sodium plumbite solution* over the escaping vapors. If it blackens, the tin itself contains a little sulfide and cannot be used for the most delicate test. Usually, however, the blackening with tin alone is so slight that an allowance can be made for it. Now add a little of the substance to be tested and a little more tin. A trace of sulfide will cause blackening of the lead acetate paper.

6. **Metallic Silver** is blackened by both free hydrogen sulfide and soluble sulfides:

$$4\,Ag + 2\,H_2S + O_2\,(air) \rightarrow 2\,H_2O + 2\,Ag_2S$$
$$4\,Ag + 2\,Na_2S + 2\,H_2O + O_2\,(air) \rightarrow 4\,NaOH + 2\,Ag_2S$$

If oxygen and water are not present, the above reactions will not take place. A piece of bright silver suspended for fourteen hours in a sulfur spring showed no sign of darkening until it had been exposed to the air for a short time.

Absolutely dry hydrogen sulfide, in the presence of absolutely dry oxygen, acts upon silver at ordinary temperatures only very slowly; it acts instantly if a trace of water is present.

To detect the presence of sulfur in insoluble sulfides, fuse with a little caustic soda (on the cover of a porcelain crucible) to form soluble sodium sulfide:

$$NiS + 2\,NaOH \rightarrow H_2O + NiO + Na_2S$$

Some sulfate is always formed by this treatment; but the aqueous solution of the melt will always contain enough alkali sulfide for any of the above tests.

7. **Methylene Blue.** — This reaction (which was recommended by Emil Fisher†) is the most sensitive of all reactions for detecting the presence of hydrogen sulfide. It is particularly suited for detecting the presence of traces of hydrogen sulfide in mineral waters, even when all other tests give negative results.

Treat the solution to be tested for hydrogen sulfide with one-tenth of its volume of concentrated hydrochloric acid, add a little dimethylparaphenylenediamine‡ sul-

* Lead acetate solution treated with enough sodium hydroxide to dissolve the lead hydroxide that forms first.

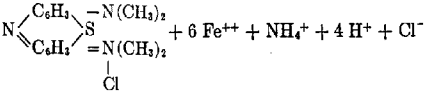
† *Ber.*, **16**, 2234.

‡ This may also be called para-aminodimethylaniline sulfate.

fate, $NH_2 \cdot C_6H_4 \cdot N(CH_3)_2 \cdot H_2SO_4$, from the point of a knife-blade, stir it into the liquid, and when it has dissolved, add one or two drops of a dilute ferric chloride solution.

The formation of methylene blue may be expressed by the following equation:

$$2\,[NH_2 \cdot C_6H_4 \cdot N(CH_3)_2 \cdot HCl] + 6\,Fe^{+++} + S^{--} \rightarrow$$



$$+ 6\,Fe^{++} + NH_4^+ + 4\,H^+ + Cl^-$$

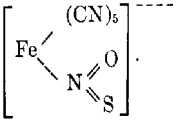
If only 0.02 mg of hydrogen sulfide is present in a liter, the blue color is distinctly apparent after half an hour's standing, while the above tests would give negative results.

If too little hydrochloric acid is present, a red coloration is obtained; this is caused by the action of ferric chloride upon a faintly acid solution of dimethyl-*p*-phenylenediamine. If considerable hydrochloric acid is present, the red coloration does not appear.

8. **Oxidizing Agents,** such as the halogens, nitric acid, chromates, permanganates, ferric salts, etc., decompose hydrogen sulfide with separation of sulfur.

9. **Sodium Azide,** NaN_3, and **Iodine** react to form sodium iodide and nitrogen gas in the presence of sulfide (cf. p. 341). The test is obtained with 0.3 γ of alkali sulfide and is valuable in the absence of thiocyanate and thiosulfate. When these are present first remove the sulfide by precipitation as CdS or ZnS and carry out the test with the well-washed precipitate; the catalysis takes place with these insoluble sulfides

$$2\,NaN_3 + I_2 \rightarrow 2\,NaI + 3\,N_2\uparrow$$

10. **Sodium Nitroprusside,** $Na_2[Fe(CN)_5(NO)] \cdot 2\,H_2O$, is colored reddish violet by S^{--} ions, but not by SH^- ions. Consequently hydrogen sulfide itself does not give this reaction, except upon the addition of caustic alkali. The reaction is very sensitive, but not so delicate as the one with an alkaline solution of a lead salt. It can be obtained, however, with 1 γ of sodium sulfide. The compound formed has the formula $Na_4[Fe(CN)_5\,NOS]$; it may be an addition compound or it may contain the anion  .

Behavior of the Sulfides on Ignition

Most sulfides remain unchanged when heated out of contact with the air; arsenic and mercuric sulfides sublime. The polysulfides lose

sulfur, which sublimes. The sulfides of gold and platinum lose sulfur, leaving the metal behind. All sulfides when heated in the air give off sulfur dioxide, which can be recognized by its odor.

The Detection of Sulfur in Non-Electrolytes is usually effected by heating the substance in a glass tube with metallic sodium (cf. p. 304), and testing the aqueous extract of the melt with sodium nitroprusside; or the residue in the tube may be treated with dilute hydrochloric acid and the escaping gas tested with lead acetate paper for hydrogen sulfide.

The following method of testing for sulfur is very certain. It depends upon the conversion of any sulfur present into sulfate ion which is tested for with barium chloride in hydrochloric acid solution. (Cf. p. 433.) The best way of converting the sulfur into sulfuric acid is to heat with concentrated nitric acid in a sealed tube (Carius method, see Vol. II) or, with difficultly volatile substances low in sulfur, by fusion with sodium peroxide in a nickel crucible. Since, however, this last oxidation often takes place with explosive violence, it is best not to use pure sodium peroxide, but to mix it with sodium potassium carbonate. Mix the substance (from 0.1 to 5 g according to the sulfur content) with ten times as much sodium potassium carbonate and three times as much sodium peroxide and heat in a nickel crucible, with the crucible inserted in a disk of asbestos board to keep the flame of the gas away from the contents; if this precaution is not taken a little sulfate is obtained from the sulfur in the gas. After cooling the melt, dissolve it in water, filter, acidify with hydrochloric acid, and test the filtrate for sulfuric acid with barium chloride.

SULFUR, S

M. P. 112.8°-119.3°. B. P. 444.5°

Occurrence. — Sulfur is found native in volcanic regions in the form of orthorhombic pyramids, and in the neighborhood of sulfur waters, being formed from the oxidation of some of the hydrogen sulfide which escapes.

Preparation and Properties. — Like the halogens, sulfur is formed by the oxidation of its hydrogen compound:

$$2\,H_2S + O_2 \rightarrow 2\,H_2O + 2\,S$$

By heating polysulfides or the sulfides of the noble metals (gold and platinum), sulfur is also obtained.

Sulfur exists in at least two liquid forms S γ and S μ (S γ is probably S_8, and S μ is said to be S_6) and in three allotropic solid modifications:

1. As *Orthorhombic Sulfur*, with a melting point of 112.8° C, obtained by crystallization from solutions below 95°. Its density is 2.06 at 0° and it melts to form S γ. The reaction monoclinic S $\rightleftarrows$ orthorhombic S takes place at 96°. Above this temperature, the monoclinic form is the more stable.

2. As *Monoclinic Sulfur*, with a melting point of 119.3° C, obtained by the solidification of molten sulfur. Its density is 1.96, and it melts to form S γ.

3. As *Amorphous Sulfur*, obtained by quickly cooling the molten sulfur after it has become viscous by heating to 250° C, or after it has become a thin liquid after heating to a higher temperature.

Both of the *crystalline* modifications of sulfur are soluble in carbon disulfide; and, by evaporating the solution, the sulfur always recrystallizes in the form of octahedrons. Amorphous sulfur is insoluble in carbon disulfide.

Commercial " flowers of sulfur " is a mixture of crystalline and amorphous sulfur, and therefore is only partly soluble in carbon disulfide.

If molten monoclinic sulfur, which can be obtained by crystallization of liquid sulfur at a temperature just below 120°, is kept for some hours at a temperature only a few degrees above its melting point, 119.3°, and is then cooled, it solidifies at 114.5°. If molten sulfur is heated, it changes from a mobile, yellow liquid to a dark red, viscous liquid and reaches a maximum viscosity at about 200°. At higher temperatures the fluidity increases but the color darkens and becomes almost black. If, at a temperature near the boiling point, 444.5°, the molten sulfur is poured into cold water, a soft, ductile, elastic mass is obtained resembling rubber. In a few hours it changes into the ordinary orthorhombic form which is the stable state at room temperatures.

In chemical behavior sulfur is intermediate between oxygen and selenium; all three elements belong in the sixth family of the periodic classification. The lowest valence of sulfur is shown in hydrogen sulfide (−2) and the highest in sulfuric acid (+6).

Sulfur burns in the air to sulfur dioxide, and, in the presence of " contact substances," such as platinum, oxide of iron, chromic oxide, etc., it is burned to sulfur trioxide also. Consequently the gas from pyrites burners always contains a mixture of the two gases.

Sulfur is insoluble in water, but soluble in hot caustic alkali, forming a thiosulfate and a sulfide:

$$6\ NaOH + 4\ S \rightarrow 3\ H_2O + Na_2S_2O_3 + 2\ Na_2S$$

By further action of sulfur the Na_2S is changed into Na_2S_2, Na_2S_5, etc.

This reaction is entirely analogous to the formation of hypochlorite and chloride by the action of chlorine upon cold dilute caustic alkali:

$$2\ NaOH + Cl_2 \rightarrow H_2O + NaOCl + NaCl$$

Sulfur dissolves on warming with an alkali sulfide, forming polysulfides:

$$Na_2S + S \rightarrow Na_2S_2$$

$$Na_2S + 4\ S \rightarrow Na_2S_5$$

Sulfur is also soluble in alkali sulfites, forming a thiosulfate:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

Hot, concentrated nitric acid, bromine and hydrochloric acid, aqua regia and a mixture of potassium chlorate and hydrochloric acid gradually attack sulfur, forming sulfuric acid.

The following fourteen acids containing sulfur are known in the form of salts; those marked with an asterisk (*) are unstable and decompose when liberated by the action of mineral acid upon one of the salts.

Hydrosulfuric (hydrogen sulfide)	H_2S
Sulfoxylic*	H_2SO_2
(Hyposulfurous*) Dithionous	$H_2S_2O_4$
Sulfurous	H_2SO_3
Sulfuric	H_2SO_4
Pyrosulfuric	$H_2S_2O_7$
Monopersulfuric (Caro's acid)	H_2SO_5
Persulfuric*	$H_2S_2O_8$
Thiosulfuric*	$H_2S_2O_3$
Dithionic	$H_2S_2O_6$
Trithionic	$H_2S_3O_6$
Tetrathionic	$H_2S_4O_6$
Pentathionic	$H_2S_5O_6$
Hexathionic*	$H_2S_6O_6$

The acid corresponding to the formula $H_2S_2O_4$ is correctly named *hyposulfurous acid.* When first discovered, the sodium salt was thought to be $NaHSO_2$, instead of $Na_2S_2O_4$ and it is still called *hydrosulfite* in the trade. The name hyposulfurous acid, however, is unfortunate because $H_2S_2O_3$ has often been given that incorrect name. To avoid these difficulties, *Chemical Abstracts* now prefers the name dithionous acid.

ACETIC ACID, $HC_2H_3O_2$*

Occurrence. — Acetic acid is found in the sap of many plants, partly free and partly in the form of its potassium or calcium salt.

Preparation. — It is formed by the dry distillation of wood or by the oxidation of alcohol. Vinegar made from cider contains 4 to 5 per cent of acetic acid.

Properties. — Anhydrous acetic acid (glacial acetic acid) solidifies below +16.6° C forming colorless, glistening plates. It has a penetrating odor, similar to that of sulfur dioxide, and is miscible with water, alcohol, and ether in every proportion. It boils at 118° C.

The aqueous solution reacts as a weak acid. The ionization constant at 25° is 1.8×10^{-5}; in 0.1-normal solution it is a little over one per cent ionized. It is a monobasic acid, and its salts, the acetates, are as a rule readily soluble in water; the silver salt is difficultly soluble.

The most important commercial salts of this acid are sodium acetate and lead acetate (sugar of lead), $Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$.

Neutral lead acetate dissolves lead oxide with the formation of soluble basic salts:

$$Pb(C_2H_3O_2)_2 + PbO + H_2O \rightarrow 2\ Pb\begin{matrix} -OH \\ -C_2H_3O_2 \end{matrix}$$

$$Pb(C_2H_3O_2)_2 + 2\ PbO \rightarrow Pb\begin{matrix} -O-Pb-C_2H_3O_2 \\ -O-Pb-C_2H_3O_2 \end{matrix}$$

The solutions of the soluble basic lead acetates, as well as that of neutral lead acetate, yield precipitates of lead carbonate when acted upon by carbon dioxide. For this reason turbid solutions are often obtained when these salts are dissolved in distilled water, because the latter frequently contains carbonic acid. If a drop of acetic acid is added to the turbid solution the precipitate disappears at once.

Reactions in the Wet Way

Use a solution of sodium acetate for the following reactions:

1. **Dilute Sulfuric Acid** sets acetic acid free from its salts; it is quite volatile and can be recognized by its odor.

2. **Concentrated Sulfuric Acid** also sets acetic acid free. If alcohol

* The organic chemist writes the symbol for acetic acid thus: CH_3COOH. In *Chemical Abstracts* the symbol Ac is used for the acetyl radical, CH_3CO, and acetic acid is written AcOH. Some chemists have used the symbol Ac to denote the acetate anion, $CH_3CO_2^-$.

is added at the same time and the mixture warmed, ethyl acetate is formed,

$$HC_2H_3O_2 + C_2H_5OH \rightarrow H_2O + \underset{\text{Ethyl acetate}}{C_2H_5 \cdot C_2H_3O_2}$$

which can be recognized by its pleasant, fruity odor.

3. **Silver Nitrate** produces, in fairly concentrated solutions, a white crystalline precipitate of silver acetate (100 ml of water dissolves 10.4 g at 20° C and 2.52 g at 80° C).

4. **Ferric Chloride** colors neutral solutions dark brown, and by boiling the diluted solution, all the iron is precipitated as basic acetate (cf. p. 213).

5. **Lanthanum Nitrate** gives with iodine, ammonia, and acetate ions a beautiful, dark blue precipitate which is probably due to adsorption of I_2 by basic lanthanum acetate. If phosphate or sulfate is present, it is best to remove it by precipitation with barium nitrate before applying the following test:

Place 1 drop of the solution to be tested on a spot plate and add 1 drop of 5 per cent $La(NO_3)_3$ solution and 1 drop of 0.01 *N* iodine solution. After a minute add 1 drop of *N* NH_4OH and allow to stand for a few minutes. A blue or bluish brown ring will form around the ammonia drop if 0.05 mg of acetate is present (Feigl).

6. **Lead Oxide,** PbO, on being heated with dilute acetic acid is dissolved, and if an excess of the oxide is used, the solution contains basic lead acetate and reacts alkaline; on cooling no crystals are obtained.

7. **Mercurous Nitrate** produces a white precipitate of mercurous acetate:

$$Hg_2^{++} + 2\,C_2H_3O_2^- \rightarrow \mathbf{Hg_2(C_2H_3O_2)_2}$$

One gram of the acetate dissolves in 133 ml of water at 15°. The precipitate is much more soluble in hot water and on cooling it crystallizes out again, appearing gray because of slight reduction in the neutral solution. Mercurous acetate dissolves in an excess of mercurous nitrate solution.

Reactions in the Dry Way

All acetates are decomposed on ignition, leaving behind either the carbonate, oxide, or the metal itself, and with the evolution of combustible vapors and gases.

The acetates of the alkalies are decomposed into carbonate and acetone:

$$2\,NaC_2H_3O_2 \rightarrow Na_2CO_3 + (CH_3)_2CO$$

The acetates of the alkaline earths always leave the metal in the form of its oxide, while the acetates of the noble metals leave a residue of the metal itself.

Cacodyl Reaction. — If a dry acetate (best an alkali acetate) is heated with arsenic trioxide, a very repulsive-smelling and extremely poisonous gas is formed, called cacodyl oxide:

$$4\,NaC_2H_3O_2 + As_2O_3 \rightarrow 2\,Na_2CO_3 + [(CH_3)_2As]_2O\uparrow + 2\,CO_2\uparrow$$

In spite of the sensitiveness of this test, it cannot always be relied on, for many other organic acids, such as butyric and valerianic acids, give similar reactions.

CYANIC ACID, HCNO

Preparation and Properties. — This very unstable acid is obtained by heating its polymer, cyanuric acid, $(HCNO)_3$; it is a colorless liquid with a very penetrating, disagreeable odor, which immediately decomposes in aqueous solution, forming ammonium bicarbonate:

$$HCNO + 2\,H_2O \rightarrow \underset{\text{Carbamic acid}}{HCO_2NH_2} + H_2O \rightarrow NH_4HCO_3$$

The salts of cyanic acid, the cyanates, are much more stable than the free acid, and may be obtained by the oxidation of cyanides.

By simply fusing potassium cyanide in the air, perceptible quantities of potassium cyanate are formed. If, however, potassium cyanide is heated with oxidizing substances, or those which can be readily reduced, it is easy to change the cyanide completely over to cyanate. The cyanates of the alkalies are stable in the dry state, but take on moisture from the air and are gradually changed into alkali bicarbonate and ammonia:

$$KCNO + 2\,H_2O \rightarrow KHCO_3 + NH_3\uparrow$$

Solubility of Cyanates. — The cyanates of the alkalies and alkaline earths are soluble in water. Silver, mercurous, lead, and copper cyanates are insoluble in water. All cyanates are soluble in nitric acid.

Reactions in the Wet Way

Use a freshly prepared, cold solution of potassium cyanate for these reactions.

1. **Dilute Sulfuric Acid** immediately sets cyanic acid free, which decomposes into ammonium salt and carbon dioxide:

$$CNO^- + H^+ \rightarrow HCNO;\ HCNO + 2\,H_2O \rightarrow NH_4^+ + HCO_3^-$$

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2\uparrow$$

Consequently a strong evolution of carbon dioxide takes place on adding the sulfuric acid. The carbon dioxide always contains small amounts of undecomposed cyanic acid, which is recognizable by its very penetrating odor. The solution will contain ammonium sulfate; if it is warmed with caustic soda, ammonia will be given off.

2. **Concentrated Sulfuric Acid** reacts similarly.

3. **Silver Nitrate** precipitates white, curdy silver cyanate,

$$KCNO + AgNO_3 \rightarrow KNO_3 + \mathbf{AgCNO}$$

soluble in ammonia and in nitric acid (difference from silver cyanide).

4. **Barium Chloride** produces no precipitation.

5. **Cobalt Acetate** is colored azure blue by a solution of potassium cyanate. The blue potassium cobaltocyanate, $K_2[Co(CNO)_4]$, dis-

covered by Blomstrand,* is formed by this reaction, and is obtained in the form of tetragonal crystals.

This blue compound dissolves in water with a blue color. If, however, it is subjected to the action of considerable water, the color disappears, the double salt being dissociated into its components:

$$K_2[Co(CNO)_4] \rightleftarrows Co(CNO)_2 + 2\,KCNO$$

If more potassium cyanate is added to the solution, which has become colorless, the blue color reappears. The same result is reached by adding alcohol.

DETECTION OF CYANATE IN THE PRESENCE OF CYANIDE

Almost all commercial potassium cyanide contains some cyanate. In order to detect the presence of cyanate in the commercial salt, the cyanide must first be expelled, for the cobalt test does not take place in the presence of cyanide.

According to E. A. Schneider,† the test is made as follows:

Dissolve 3 to 5 g of the potassium cyanide in 30 to 50 ml of cold water and pass carbon dioxide into the solution for 60 to 90 minutes; the hydrocyanic acid is expelled, and potassium bicarbonate is formed, while the potassium cyanate is not affected perceptibly:

$$KCN + H_2CO_3 \rightarrow HCN\uparrow + KHCO_3$$

Take 1 ml of the solution, add 25 ml of absolute alcohol (to precipitate potassium bicarbonate), and filter. Treat the alcoholic filtrate with a few drops of acetic acid and then add a few drops of alcoholic cobalt acetate solution.

If the original cyanide contained 0.5 per cent of potassium cyanate, the blue color can be distinctly recognized, but alkali thiocyanates give the same reaction.

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* *J. prakt. Chem.*, [2], **3**, 206.

† *Ber.*, **1895**, p. 1540.

HYPOPHOSPHOROUS ACID, H_3PO_2

Preparation and Properties. — Hypophosphorous acid is obtained by the decomposition of its barium salt with sulfuric acid, or of its calcium salt with oxalic acid. It is a sirup in concentrated solutions, and, like phosphorous acid, is changed on heating out of contact with the air into phosphoric acid and spontaneously inflammable phosphine gas. The acid is monobasic, and is a moderately strong acid although only one of the hydrogen atoms is replaceable by metals. The structural formula $O{=}P{-}H$ (with OH and H attached to P) is usually assigned to hypophosphorous acid, and the assumption is made that only the hydrogen atom that is attached to oxygen is replaceable. The phosphorus atom is positive toward oxygen and negative toward the hydrogen atoms attached to it; this gives to the phosphorus atom a polarity (sum of the positive and negative valences) of +1. Sodium hypophosphite, NaH_2PO_2, is an excellent reducing agent. It reduces stannic chloride, palladium salts, iodates, and tellurites under suitable conditions. The salts of hypophosphorous acid are obtained by boiling phosphorus with dilute alkali, whereby phosphine is given off:

$$2\,P_4 + 3\,Ba(OH)_2 + 6\,H_2O \rightarrow 3\,Ba(H_2PO_2)_2 + 2\,PH_3\uparrow$$

$$P_4 + 3\,KOH + 3\,H_2O \rightarrow 3\,K(H_2PO_2) + PH_3\uparrow$$

The phosphine thus obtained is spontaneously combustible owing to the presence of small quantities of liquid phosphine, P_2H_4; it is, however, mixed with considerable hydrogen because the alkali reacts upon the alkali hypophosphite with evolution of hydrogen. See 5, page 363.

Solubility of Hypophosphites. — All hypophosphites are soluble in water.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid** reacts with hypophosphites only on warming, and is reduced to sulfur dioxide, which can be recognized by its odor.

3. **Silver Nitrate** gives white silver phosphite which, even at room temperature, is reduced to metallic silver, sometimes with and sometimes without the evolution of hydrogen, according to the relative amounts of the substances reacting:

$$2\,H_2PO_2^- + 2\,Ag^+ + 4\,H_2O \rightarrow 2\,H_3PO_4 + 2\,Ag + 3\,H_2\uparrow$$

$$H_2PO_2^- + 4\,Ag^+ + 2\,H_2O \rightarrow H_3PO_4 + 4\,Ag + 3\,H^+$$

4. **Ammonium Molybdate** and a few drops of sulfurous acid solution give a dark blue precipitate or a blue color. This very sensitive reaction is hindered by the presence of hydrogen sulfide, thiosulfate, chlorate and stannous chloride.

5. **Concentrated Alkali Hydroxide.** — By boiling with concentrated caustic alkali, the hypophosphites are oxidized, with evolution of hydrogen, to phosphates:

$$H_2PO_2^- + 2\,OH^- \rightarrow PO_4^{---} + 2\,H_2\uparrow$$

6. **Barium Chloride, Calcium Chloride,** and **Lead Acetate** cause no precipitation.

7. **Copper,* Mercury,** and **Gold Salts** are reduced to metal.

8. **Mercuric Chloride** added in excess to a hot solution causes precipitation of mercurous chloride:

$$4\,HgCl_2 + H_2PO_2^- + 2\,H_2O \rightarrow 2\,Hg_2Cl_2 + 3\,H^+ + H_3PO_4 + 4\,Cl^-$$

9. **Zinc** in dilute sulfuric acid solution reduces hypophosphorous acid to phosphine (see Phosphorous Acid).

Reactions in the Dry Way

By ignition phosphate and phosphine are obtained:

$$2\,H_3PO_2 \rightarrow H_3PO_4 + PH_3\uparrow$$

$$4\,NaH_2PO_2 \rightarrow Na_4P_2O_7 + H_2O\uparrow + 2\,PH_3\uparrow$$

$$2\,Ca(H_2PO_2)_2 \rightarrow Ca_2P_2O_7 + H_2O\uparrow + 2\,PH_3\uparrow$$

* With copper the reduction may go so far that copper hydride is formed. Cf. Wurtz, *Compt. rend.*, **18**, 102.

HYDRAZOIC ACID, HN_3

Properties. — Hydrazoic acid is a colorless, mobile liquid with an odor like that of phosphine. Its constitution may be represented by the formula

$$\begin{array}{l} H - N - N \\ \qquad \backslash N \diagup \end{array}$$

Its vapors attack the mucous membrane, and they explode violently when brought in contact with a flame. The aqueous solution is colorless, and the acid is of approximately the same strength as acetic acid, having the ionization constant 1.9×10^{-5} at 25°. The salts of this acid are called azides. Moreover, just as chlorine can be made to replace the OH group of an organic acid to form an acid chloride, similarly the azide group may be introduced instead of the OH of the carboxyl radical, forming organic azides.

Hydrazoic acid and all the azides are more or less explosive so that work with them is not unattended with danger. On heating, or by percussion, very violent explosions are obtained.

Hydrazoic acid dissolves metals with the formation of azides and evolution of hydrogen.

$$2\,HN_3 + Zn \rightarrow Zn(N_3)_2 + H_2\uparrow$$

but a part of the hydrazoic acid is reduced to hydrazine, $NH_2{\cdot}NH_2$, and ammonia:

$$3\,Zn + 7\,HN_3 \rightarrow 3\,Zn(N_3)_2 + NH_3\uparrow + N_2H_4$$

Other reducing agents accomplish this formation of ammonia and hydrazine. Fuming hydriodic acid causes the formation of nitrogen, ammonia, and iodine:

$$HN_3 + 2\,HI \rightarrow N_2\uparrow + NH_3 + I_2$$

Most azides are soluble in water.

Oxidizing agents, especially iodine, cause the formation of nitrogen gas:

$$2\,HN_3 + I_2 \rightarrow 2\,HI + 3\,N_2\uparrow$$

Ceric salts are well suited to cause decomposition of hydrazoic acid; cerous salts and nitrogen are obtained.

Reactions in the Wet Way

1. **Silver Nitrate** in neutral solution gives a white precipitate of silver azide:

$$Ag^+ + N_3^- \rightarrow AgN_3$$

The precipitate resembles silver chloride in appearance but it is soluble in dilute nitric acid.

2. **Mercurous Nitrate** and **Lead Nitrate** cause similar azides to precipitate.

3. **Ferric Chloride** gives a characteristic red coloration.

GROUP III

Silver Nitrate produces a white precipitate, soluble in nitric acid.
Barium Chloride does the same.

SULFUROUS ACID, H_2SO_3

Occurrence and Preparation. — Sulfur dioxide, the anhydride of sulfurous acid, is found in the exhalations of active volcanoes, and is formed by the combustion of sulfur or sulfides in the air,

$$S + O_2 \rightarrow SO_2\uparrow$$
$$4\,FeS_2 + 11\,O_2 \rightarrow 2\,Fe_2O_3 + 8\,SO_2\uparrow$$

or by the reduction of sulfuric acid on heating with sulfur, sulfides, carbon, organic substances, and metals:

$$2\,H_2SO_4 + S \rightarrow 2\,H_2O + 3\,SO_2\uparrow$$
$$2\,H_2SO_4 + C \rightarrow 2\,H_2O + CO_2\uparrow + 2\,SO_2\uparrow$$
$$2\,H_2SO_4 + Cu \rightarrow 2\,H_2O + CuSO_4 + SO_2\uparrow$$

Mercury, silver, tin, etc., act the same as copper. Sulfur dioxide is also formed by the decomposition of sulfites and thiosulfates with stronger acids:

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$
$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + S + H_2O + SO_2\uparrow$$

Sulfurous acid may be prepared for laboratory purposes by placing a concentrated solution of sodium bisulfite in a flask and allowing concentrated sulfuric acid to drop upon it. A steady stream of sulfur dioxide will be evolved without warming.

Properties. — Sulfur dioxide is a colorless gas, having the penetrating odor peculiar to burning sulfur, and is readily soluble in water and alcohol: 1 volume of water at 15° C dissolves 45.36 volumes of SO_2; 1 volume of alcohol at 15° C dissolves 116 volumes of SO_2.

The aqueous solution contains molecules of SO_2, $SO_2{\cdot}6\,H_2O$, and a small quantity of sulfurous acid, H_2SO_3. The acid cannot be isolated, as it decomposes on evaporation into water and sulfur dioxide; consequently the free acid is known only in aqueous solution. It is an acid of moderate strength having an ionization constant of 1.7×10^{-2} for the primary ionization and of 10^{-7} for the secondary ionization. By neutralization of this solution with alkali hydroxides or carbonates, the comparatively stable sulfites are obtained. *In solution, sulfites are gradually oxidized to sulfates by dissolved oxygen. Sulfurous acid is a good reducing agent.*

Solubility of Sulfites. — The sulfites of the alkalies are readily soluble in water; the remaining sulfites are difficultly soluble or insoluble in water, but all are soluble in hydrochloric acid.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** evolves sulfur dioxide, in the cold, from all sulfites, the gas being easily recognized by its odor.

2. **Concentrated Sulfuric Acid** reacts in the same way, but much more energetically.

3. **Silver Nitrate** produces, in neutral solutions of sulfites or in an aqueous solution of sulfurous acid, a white crystalline precipitate of silver sulfite,

$$SO_3^{--} + 2\,Ag^+ \rightarrow Ag_2SO_3$$

soluble in an excess of alkali sulfite, forming sodium argentisulfite:

$$Ag_2SO_3 + Na_2SO_3 \rightarrow 2\,Na[AgSO_3]$$

By boiling this solution the silver is precipitated as a gray metal:

$$2\,[AgSO_3]^- \rightarrow SO_4^{--} + SO_2\uparrow + 2\,Ag$$

If water containing silver sulfite in suspension is boiled, half the silver is reduced to metal, the other half going into solution as sulfate:

$$2\,Ag_2SO_3 \rightarrow Ag_2SO_4 + SO_2\uparrow + 2\,Ag$$

Silver sulfite is soluble in ammonia and in nitric acid.

4. **Barium Chloride** produces no precipitation in an aqueous solution of sulfurous acid, but in neutral sulfite solutions white barium sulfite is precipitated,

$$SO_3^{--} + Ba^{++} \rightarrow BaSO_3$$

readily soluble in cold, dilute nitric acid. By boiling the solution, barium sulfate is formed slowly and separates out. Since sulfites in aqueous solution gradually change to sulfates, commercial sulfites usually contain sulfate. In this case the precipitate produced by barium chloride in acid solution is barium sulfate, which is insoluble in dilute nitric or hydrochloric acid. If the barium sulfate is filtered off and the filtrate is treated with chlorine or bromine water, another white precipitate of barium sulfate is formed, provided a sulfite was originally present:

$$SO_3^{--} + Cl_2 + Ba^{++} + H_2O \rightarrow 2\,H^+ + 2\,Cl^- + BaSO_4$$

5. **Chromic Acid** is reduced to green chromic salt:

$$2\,CrO_4^{--} + 3\,SO_3^{--} + 10\,H^+ \rightarrow 2\,Cr^{+++} + 3\,SO_4^{--} + 5\,H_2O$$

6. **Gold Solutions** are reduced to free metal.

7. **Hydrogen Sulfide** decomposes sulfurous acid in dilute solutions. The principal reaction may be expressed by the equation:

$$H_2SO_3 + 2\,H_2S \rightarrow 3\,H_2O + 3\,S$$

but pentathionic acid, $H_2S_5O_6$, and possibly other thionic acids, may

be formed at the same time:

$$5\,H_2SO_3 + 5\,H_2S \rightarrow H_2S_5O_6 + 9\,H_2O + 5\,S$$

8. **Iodine Solution** is decolorized by sulfurous acid:

$$SO_3^{--} + H_2O + I_2 \rightarrow 2\,H^+ + 2\,I^- + SO_4^{--}$$

Chlorine or bromine water causes a similar reaction.

9. **Lead Salts** precipitate white lead sulfite, soluble in cold dilute nitric acid; but on boiling the solution lead sulfate is precipitated.

10. **Malachite Green** is decolorized by sulfites. Place 1 drop of a solution containing 10 mg of the dyestuff in 500 ml of water on a spot plate and mix with 1 drop of the neutral solution to be tested. If 1γ of SO_2 is present, decolorization takes place.

11. **Mercuric Chloride** is unaffected by sulfurous acid at ordinary temperatures; but, on boiling, it is reduced to mercurous chloride,

$$2\,HgCl_2 + SO_3^{--} + H_2O \rightarrow 2\,H^+ + 2\,Cl^- + SO_4^{--} + \mathbf{Hg_2Cl_2}$$

and on adding more sulfurous acid, the mercurous salt is reduced to gray metallic mercury.

12. **Mercurous Nitrate** is immediately acted upon by free sulfurous acid and by alkali sulfite solutions, with the formation of a black precipitate.

13. Acid **Potassium Permanganate Solution** is also decolorized; sulfuric and dithionic acids are formed in varying amounts according to the temperature and concentration.

Under certain conditions the reaction can take place according to the following equation:

$$2\,MnO_4^- + 6\,SO_3^{--} + 8\,H^+ \rightarrow 2\,Mn^{++} + 4\,SO_4^{--} + S_2O_6^{--} + 4\,H_2O$$

Under other conditions, however, the sulfurous acid can be completely oxidized to sulfuric acid. Consequently, sulfurous acid cannot be determined by means of potassium permanganate.

14. **Sodium Nitroprusside** and **Zinc Sulfate.** — If a neutral sulfite solution is treated with a dilute solution of sodium nitroprusside, a faint pink coloration is produced. If, however, considerable zinc sulfate is added, the coloration becomes a distinct red. The reaction is still more sensitive if a little potassium ferrocyanide is added, a red precipitate being formed (difference from thiosulfuric acid). This reaction, although very delicate, is not so reliable as the precipitation with strontium chloride.

15. **Strontium** and **Calcium Salts** behave similarly to the barium salt.

The sulfites of the alkaline earths vary in their solubilities in sulfurous acid and in water. Calcium sulfite readily dissolves in an excess of sulfurous acid, forming calcium bisulfite:

$$CaSO_3 + H_2SO_3 \rightarrow Ca(HSO_3)_2$$

On boiling this solution, sulfur dioxide escapes, and calcium sulfite is reprecipitated. The strontium salt also dissolves in sulfurous acid, but more difficultly; the barium salt is practically insoluble in sulfurous acid.

SOLUBILITY OF THE ALKALINE EARTH SULFITES IN WATER

One gram calcium sulfite dissolves in 800 ml water at 18° C.
One gram strontium sulfite dissolves in 30,000 ml water at 18° C.
One gram barium sulfite dissolves in 46,000 ml water at 18° C.

Advantage is taken of the difficult solubility of strontium sulfite in detecting sulfurous acid in the presence of thiosulfuric acid (which see).

16. **Zinc,** in dilute hydrochloric acid solution, reduces sulfurous acid to hydrogen sulfide, which can be recognized by its odor and by its turning lead acetate paper black. Zinc and aqueous sulfurous acid also react to form *hydrosulfurous* acid, $H_2S_2O_4$, a very strong reducing agent:

$$Zn + 2\,SO_3^{--} + 6\,H^+ \rightarrow Zn^{++} + H_2S_2O_4 + 2\,H_2O$$

Reactions in the Dry Way

The sulfites of the alkalies, when heated out of contact with the air, are changed to sulfate and sulfide:

$$4\,Na_2SO_3 \rightarrow 3\,Na_2SO_4 + Na_2S$$

By heating an alkali sulfite in the closed tube this reaction takes place, and there is no sublimate of sulfur (difference from thiosulfates). If the melt is treated with hydrochloric acid after cooling, hydrogen sulfide is given off freely.

The remaining sulfites are changed, on being heated out of contact with the air, into sulfur dioxide and oxide or metal:

$$CaSO_3 \rightarrow CaO + SO_2\uparrow$$

$$2\,Ag_2SO_3 \rightarrow 4\,Ag + 2\,SO_2\uparrow + O_2\uparrow$$

If a sulfite is heated with sodium carbonate on charcoal, sodium sulfide is formed. If the melt is placed upon a bright silver coin and moistened with water, the silver is blackened, owing to the formation

of black silver sulfide (hepar reaction):

$$2\,\mathbf{Na_2SO_3} + 3\,\mathbf{C} \rightarrow 3\,CO_2\uparrow + 2\,\mathbf{Na_2S}$$

$$2\,Na_2S + 4\,\mathbf{Ag} + 2\,H_2O + O_2 \rightarrow 4\,NaOH + 2\,\mathbf{Ag_2S}$$

This hepar reaction takes place with all sulfur compounds, and therefore shows simply the presence of sulfur. The oxygen required in the above reaction is obtained from the atmosphere.

CARBONIC ACID, H_2CO_3

Occurrence. — Like sulfurous acid, pure carbonic acid does not exist; it is known only in aqueous solution. Its anhydride, CO_2, is formed by the combustion of carbon and of carbonaceous matter of all kinds, and is found therefore very widely distributed in nature (in small amounts in the atmosphere, and in enormous amounts in volcanic regions, streaming out from fissures in the earth). Carbon dioxide occurs also in many mineral waters, and (in the liquid state) is found enclosed in quartz, feldspar, etc. As carbonate it exists in enormous quantities as limestone, marble, aragonite, dolomite, etc.

Pure air contains 0.035–0.040 per cent of CO_2. In dwelling places the amount increases considerably, owing to breathing and other forms of combustion. If 3 or 4 per cent is present, as sometimes in mines, breathing becomes difficult, and the miner's lamp begins to burn faintly.

Properties. — Carbon dioxide is a colorless, odorless, slightly acid-tasting gas, with density 1.52. Being, therefore, one and one-half times as heavy as air, it can be poured from one vessel into another. Carbon dioxide does not support combustion; a burning candle goes out in air containing 8 to 10 per cent of this gas.*

Carbon dioxide gas is not very soluble in water. At 15° and 760 mm pressure, 1 l of water dissolves its own volume of gas. At higher temperatures it is less soluble and it is easy to expel carbon dioxide from a solution. In the aqueous solution, the following equilibria exist

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$
$$HCO_3^- \rightleftarrows H^+ + CO_3^{--}$$

The ionization constant for the primary ionization of carbonic acid is 0.0_63, and for the secondary ionization it is $0.0_{10}5$. According to these values, the primary ionization of carbonic acid takes place to about 0.1 per cent and there is present in a liter of saturated carbon dioxide solution at 15° only about 0.0006 mole of hydrogen ions. The secondary ionization, upon which the quantity of CO_3^{--} ions present depends, takes place only to a negligible extent.

When a strong acid is added to the solution, even the primary ionization of carbonic acid is repressed almost completely. Similarly, when hydrogen ions are added to a carbonate, carbon dioxide is formed, even with acetic acid, and the carbon dioxide is easily expelled by heating. Hydrocyanic acid, hydrogen sulfide, and boric acid are the only common acids that do not decompose carbonates.

The salts of carbonic acid, the carbonates, are formed:

1. By passing carbon dioxide gas into a solution of a metallic hydroxide:

$$2\,NaOH + CO_2 \rightarrow H_2O + Na_2CO_3$$
$$Ba(OH)_2 + CO_2 \rightarrow H_2O + BaCO_3$$

---

* Carbon dioxide not only fails to support combustion, but it tends to prevent it — hence its use in fire extinguishers. Being formed by the combustion of carbon, it will tend to stop the reaction much better than an inert gas, as the mass-action principle shows.

2. By the action of carbon dioxide upon cyanides, sulfides, and borates of the alkalies and alkaline earths.

3. By the ignition of alkali salts of organic acids (cf. pp. 283, 358).

An illustration of the preparation of large amounts of carbonate is the production of potash by burning parts of plants (wood, for example, or the residue from the manufacture of beet sugar, which is particularly rich in potassium salts).

Solubility of Carbonates. — Of the normal carbonates, only those of the alkalies are soluble in water; and their aqueous solutions react alkaline, owing to hydrolytic decomposition:

$$Na_2CO_3 + H_2O \rightleftarrows 2\,Na^+ + OH^- + HCO_3^-$$

The aqueous solution of the carbonates of the alkalies, therefore, behaves as if it were a solution of caustic alkali and alkali bicarbonate.

Many carbonates dissolve in an excess of carbonic acid, forming bicarbonates, particularly the alkaline earth carbonates:

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

A solution of calcium bicarbonate on boiling is decomposed into water and carbon dioxide, and calcium carbonate is reprecipitated:

$$Ca(HCO_3)_2 \rightarrow H_2O + CO_2\uparrow + CaCO_3$$

Nearly all samples of drinking water contain calcium or magnesium bicarbonate; they become turbid, therefore, on boiling (boiler scale). Dilute, cold mineral acids decompose all carbonates with effervescence (due to evolution of carbon dioxide gas).

The native carbonates of magnesium and iron (magnesite, siderite, and dolomite) do not effervesce if a lump of the mineral is treated with cold dilute mineral acids, but when reduced to a fine powder they are more readily acted upon; on warming, all carbonates dissolve readily in acid.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** decomposes all carbonates with effervescence; except with magnesite, siderite, and dolomite, the reaction takes place in the cold.

Since the atmosphere always contains carbon dioxide gas, particularly in a laboratory where many gas flames are burning, considerable caution is necessary in testing for a small quantity of carbonic acid. In the first place, if the substance does not effervesce with acid, there is no need to make the test. Moreover, carbon dioxide is odorless, and it is absurd to think that effervescence implies the presence of a carbonate when the escaping gas has the odor of hydrogen sulfide or sulfur dioxide.

A simple method of testing is as follows: Place about 1 g of the powdered solid in a test tube, cover it with about 10 ml of water, and boil for about a minute. This serves to expel the air from the substance and from the water. Add a little 6-normal hydrochloric acid, and watch closely to see if there is any sign of effervescence. If there is effervescence notice whether the escaping gas has any odor. Dip two stirring rods into barium hydroxide solution, place one of the rods between the second and third finger and the other between the third and fourth and hold one of the rods inside the test tube, without touching the sides, and the other rod outside. If a carbonate is present, the barium hydroxide on the rod inside the test tube will become turbid faster than that on the rod held in the air. This test is of no value, however, in the presence of a sulfite, which will also cause barium hydroxide to become turbid.

The above test naturally fails to detect traces of carbonate with certainty, but it is satisfactory for all ordinary work except when a sulfite is present. To detect traces of carbonate, even in the presence of a sulfite, the following procedure is useful. Fit a 100-ml flask with a rubber stopper containing two holes. Through one hole insert a small dropping funnel so that it reaches nearly to the bottom of the flask. Through the other hole insert a right-angled glass tube which serves to lead the escaping gas to a second flask, containing about 5 g of chromic acid anhydride, CrO_3, dissolved in a little water and 25 ml of 6-normal sulfuric acid. This will serve to oxidize any sulfurous acid or hydrogen sulfide that may be set free. Arrange the tubes in this second flask so that the gas passes down to the bottom of the solution and leaves the flask through an exit tube which just reaches below the rubber stopper. Connect this flask in the same way with a third flask, and connect the exit tube from this flask with a drying tube filled with soda-lime, to prevent carbon dioxide getting in from the air. Place the powdered substance in the first flask and cover it with 25 ml of water. With the third flask empty, conduct a stream of air free from carbon dioxide through the apparatus for ten minutes while heating the water in the first flask. This is best accomplished by applying suction at the end of the train and drawing the air through soda-lime in a drying tube which is placed in a rubber stopper that fits the neck of the dropping funnel. Instead of soda-lime, caustic potash solution (1 : 2) may be used to remove the carbon dioxide from the air. When the carbon dioxide has been expelled from the apparatus, close the stopcock in the dropping funnel, take away the flame, and quickly add about 25 ml of barium hydroxide solution to the last flask. With the apparatus all connected, introduce 25 ml of 6-normal sulfuric acid into the dropping funnel and allow it to run slowly into the flask containing the substance. If not enough gas is evolved to produce a turbidity in the barium hydroxide solution, apply gentle suction as before. After a slight vacuum has been produced, *carefully* open the stopcock of the dropping funnel, with the soda-lime tube in place, and gradually heat the sulfuric acid to boiling. Continue drawing air through the apparatus for fifteen minutes if necessary. If a very slight turbidity is obtained in the barium hydroxide solution it is best to run a blank on the apparatus with all the reagents, and then repeat the experiment. If the test does not give a decided result, the presence of carbonate should never be reported.

In this test the chromic acid, which is added to oxidize the sulfurous acid, may be replaced by other oxidizing agents, *e.g.*, hydrogen peroxide or iodine.

2. **Concentrated Sulfuric Acid** reacts in the same way as dilute sulfuric acid, only more violently.

3. **Silver Nitrate** precipitates white silver carbonate, which becomes yellow on the addition of an excess of the reagent. On boiling with considerable water, the carbonate is partly decomposed into brown silver oxide and carbon dioxide; but the carbonic acid is not expelled completely except by heating to 200°. Silver carbonate is very soluble in ammonia and in nitric acid.

4. **Barium Chloride** precipitates white, voluminous barium carbonate, in the cold, which gradually on standing, but more quickly on warming, becomes crystalline and denser. The precipitate dissolves readily in dilute acids.

5. **Lead Chloride** added to an aqueous solution of alkali carbonate or bicarbonate gives a milky, white precipitate of lead carbonate. Free carbonic acid hinders the reaction, and acetic acid dissolves the precipitate.

6. **Nessler's Reagent** will not give the ammonia test in the presence of free carbonic acid or of bicarbonates. This test may be used for the detection of free carbonic acid or of bicarbonate in solution.

7. **Rosolic Acid,** $C{<}\begin{matrix}C_6H_3{<}\begin{matrix}CH_3\\OH\end{matrix}\\C_6H_4OH\\C_6H_4O\end{matrix}$, in 0.2 per cent alcoholic solution which has been treated with barium hydroxide solution until a red color begins to appear is decolorized by free carbonic acid.

Behavior of Carbonates on Ignition

The carbonates of the alkalies melt with but slight decomposition. Barium carbonate is not decomposed on charcoal before the blowpipe, and does not melt; only at a white heat is it decomposed into infusible barium oxide and carbon dioxide. All remaining carbonates are decomposed at the temperature of the blowpipe into oxide and carbon dioxide. The oxides of the noble metals break down into metal and oxygen.

PERCARBONIC ACID, $H_2C_2O_6$

Properties. — Free percarbonic acid is not known, but its potassium salt is stable in the dry state. When exposed to moisture it decomposes into hydrogen peroxide and potassium bicarbonate:

$$K_2C_2O_6 + 2\,H_2O \rightarrow H_2O_2 + 2\,KHCO_3$$

If the salt, which is characterized by its pale blue color, is placed in considerable cold, dilute sulfuric acid, it dissolves with evolution of carbon dioxide and formation of potassium acid sulfate and hydrogen peroxide. The solution gives all the characteristic reactions of hydrogen peroxide.

To distinguish between percarbonic acid and hydrogen peroxide, dissolve 10 g of potassium iodide in water and add 0.1 to 0.3 g of the finely powdered substance. If potassium percarbonate is present, iodine is at once liberated:

$$C_2O_6^{--} + 2\,I^- \rightarrow 2\,CO_3^{--} + I_2$$

If only potassium bicarbonate and hydrogen peroxide are present, the liberation of iodine will take place much more slowly.

Silver nitrate and **barium chloride**, when treated with a percarbonate, give white precipitates which are soluble in dilute nitric acid.

Potassium permanganate is decolorized by percarbonates and much gas is evolved; in neutral solutions manganese dioxide is precipitated:

$$3\,C_2O_6^{--} + 2\,MnO_4^- \rightarrow 4\,CO_3^{--} + 2\,CO_2\uparrow + 2\,\mathbf{MnO_2} + 3\,O_2\uparrow$$

$$5\,C_2O_6^{--} + 2\,MnO_4^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 10\,CO_2\uparrow + 5\,O_2\uparrow + 8\,H_2O$$

BORIC (BORACIC) ACID, H_3BO_3

Occurrence. — Boric acid is found native as sassolite; in the form of its sodium salt, as borax or tinkal, $Na_2B_4O_7 \cdot 10\ H_2O$; as boracite, $2\ Mg_3B_8O_{15} \cdot MgCl_2$; and in many silicates, such as axinite, tourmaline, datolite, etc.

Properties. — Crystallized boric acid forms colorless flakes, with a mother-of-pearl luster, which are soluble in water (100 parts water dissolve 4 parts of boric acid at 15°, and 33 parts at 100°). The aqueous solution reacts acid, and is a poor conductor of electricity; the ionization constant is 1.7×10^{-9} at 18° and 2.3×10^{-9} at 25° for the primary ionization.

By heating boric acid to 100°, it loses one molecule of water and is changed to metaboric acid, HBO_2. The latter loses more water when heated to 160°, forming pyroboric acid, $H_2B_4O_7$, which, on ignition, loses all its water, being changed to the anhydride of boric acid, boron trioxide, which remains as a difficultly volatile, hygroscopic glass.

The salts of boric acid, the borates, are derived from the meta- and pyroboric acids. The salts of the ortho acid, H_3BO_3, are not known in the pure state.

In a few exceptional reactions boron acts as a metal, forming $B(HSO_3)_3$, $(BO)_2SO_4$, BF_3, BPO_4, etc. The last compound is insoluble in water and dilute acids, but dissolves readily in caustic alkalies.

Solubility of Borates. — The borates of the alkalies dissolve in water, and the solution reacts alkaline.

A concentrated solution of borax behaves as if it contained sodium metaborate, free boric acid, and a small amount of caustic alkali:

$$Na_2B_4O_7 + 3\ H_2O \rightleftarrows 2\ NaBO_2 + 2\ H_3BO_3$$
$$NaBO_2 + 2\ HOH \rightleftarrows NaOH + H_3BO_3$$

The more dilute the solution, the greater the extent to which the hydrolysis represented by the second equation will take place; so that a very dilute solution of borax will react as if it contained simply sodium hydroxide and free boric acid.

A solution of an alkali borate will behave differently toward reagents, therefore, according to its concentration and temperature The remaining borates are difficultly soluble in water, but readily soluble in acids and in ammonium chloride solution.

Reactions in the Wet Way

For these reactions use a borax solution.

1. **Dilute Sulfuric Acid.** — No reaction. Sulfuric or hydrochloric acid added to a concentrated aqueous solution of a borate often precipitates boric acid.

2. **Concentrated Sulfuric Acid.** — No visible reaction. Most borates are decomposed by sulfuric acid, setting free boric acid, which is capable of coloring the non-luminous gas flame with a characteristic green tinge.

3. **Concentrated Sulfuric Acid and Alcohol.** — In an alkali or alkaline earth borate is treated in a small dish with methyl alcohol, then with concentrated sulfuric acid, the mixture stirred, and the alcohol lighted, a green-bordered flame will appear, as a result of the formation of boric acid methyl ester, $B(OCH_3)_3$. The test can also be made with ethyl alcohol, in which case ethyl borate, $B(OC_2H_5)_3$, is formed.

A better method is the following:

Place about 0.2 g of the solid substance, or the residue obtained by evaporating a solution which has been made alkaline with NaOH, in a 6-in. test tube to which is fitted a 2-hole rubber stopper carrying tubing like that of a wash bottle, except that the short tube is provided with a capillary on the outside and the tube through which one blows ends near the bottom of the test tube. Add 1 ml of concentrated H_2SO_4 and carefully introduce 6 ml of methyl alcohol, CH_3OH. Blow through the liquid and cause the escaping vapor to come in contact with a colorless Bunsen flame. If boric acid is present, methyl borate will be formed and the vapors of methyl borate impart the characteristic green color to the flame. When the test is made in this way, Ba and Cu do not interfere.

4. **Silver Nitrate** produces, in moderately concentrated, cold borax solutions, a white precipitate of silver metaborate:

$$Na_2B_4O_7 + 3\ H_2O + 2\ AgNO_3 \rightarrow 2\ NaNO_3 + 2\ H_3BO_3 + 2\ \mathbf{AgBO_2}$$

On warming, a brown precipitate of silver oxide is obtained:

$$2\ \mathbf{AgBO_2} + 3\ H_2O \rightarrow 2\ H_3BO_3 + \mathbf{Ag_2O}$$

From very dilute solutions, in the cold, silver nitrate produces a brown precipitate of silver oxide.

Silver borate is soluble in ammonia and in nitric acid.

5. **Barium Chloride** produces, in fairly concentrated solutions, a white precipitate of barium metaborate:

$$Na_2B_4O_7 + BaCl_2 + 3\ H_2O \rightarrow 2\ NaCl + 2\ H_3BO_3 + \mathbf{Ba(BO_2)_2}$$

soluble in an excess of barium chloride and in ammonium chloride.

6. **Calcium and Lead Salts** behave like barium chloride.

7. **Mercuric Chloride** produces a red precipitate of basic mercuric salt. If considerable free boric acid is present there is no precipitation. The precipitate is soluble in dilute acid.

8. **Turmeric.** — If a piece of turmeric paper is placed in a solution of free boric acid, apparently no change will take place unless considerable quantities of boric and sulfuric acids are present, but if the paper is dried, it becomes reddish brown. If the brown paper is again dipped in the solution of boric acid, the color remains, which is also true if the paper is dipped in a dilute sulfuric or hydrochloric acid solution (difference from the alkali test with turmeric paper). If the reddish

brown paper is moistened with caustic soda or potash solution, the paper becomes bluish black, or, if only a small amount of boric acid is present, grayish blue.

The shade and intensity of the color vary both with the amount of turmeric and with the amount of boric acid; with a very little boric acid, turmeric, and very dilute caustic soda solution a nearly pure violet color is obtained, and with considerable boric acid and stronger alkali, a greenish black color.

Borate solutions, when acidified with dilute hydrochloric acid, give the above reaction. This sensitive and convenient test for boric acid must be used with caution, for acid solutions of titanic, tantalic, columbic, and molybdic acids, and zirconia also color turmeric paper brown.

The reaction is much more sensitive if, instead of the turmeric paper itself, an alcoholic solution of turmeric is used. Place 2 or 3 drops of the yellow solution in a porcelain dish, add the solution to be tested for boric acid, acidify with acetic acid, and evaporate to dryness on the water-bath. If as much as 0.02 mg of B_2O_3 is present, the residue is colored a distinct reddish brown, while 0.002 mg suffices to cause a visible reaction (F. Henz).

Behavior of Borates on Ignition

The hydrated borates of the alkalies melt with effervescence, forming a colorless glass.

This glass has the property of dissolving many metallic oxides when heated, whereby metaborates are formed which are often very characteristically colored (borax beads); thus copper oxide is dissolved, forming a blue glass:

$$Na_2B_4O_7 + CuO \rightarrow 2\,NaBO_2 + Cu(BO_2)_2$$

If this bead is heated in the reducing flame (*i.e.*, with carbon) two things can happen:

(*a*) The colored cupric salt is reduced to colorless cuprous salt:

$$4\,NaBO_2 + 2\,Cu(BO_2)_2 + C \rightarrow CO\uparrow + Na_2B_4O_7\uparrow + 2\,NaBO_2 + Cu_2(BO_2)_2$$

(*b*) The cupric salt is reduced to metallic copper, so that the bead appears reddish brown and opaque:

$$4\,NaBO_2 + 2\,Cu(BO_2)_2 + 2\,C \rightarrow 2\,CO\uparrow + 2\,Na_2B_4O_7 + 2\,Cu$$

PERBORIC ACID, HBO_3

All the perborates are hydrolyzed to a greater or less extent when in contact with water; the aqueous solutions all give the characteristic reactions of hydrogen peroxide and of the metaborate ion.

$$BO_3^- + H_2O \rightarrow BO_2^- + H_2O_2$$

The typical reactions of the perborate anion are based upon its oxidizing power.

Reactions in the Wet Way

1. **Manganous, Nickelous,** and **Cobaltous** nitrate or sulfate solutions give black precipitates of MnO_2, $Ni(OH)_3$, and $Co(OH)_3$.

2. **Potassium Dichromate** gives blue perchromic acid, soluble in ether (cf. p. 196). **Chrome alum** solution also gives the blue color when treated with perborate and shaken with ether (difference from percarbonic acid).

3. **Potassium Iodide** gives free iodine only in acid solutions.

4. **Potassium Permanganate** is decolorized; black manganese dioxide is precipitated unless the solution is kept acid.

5. **Titanium Trichloride** gives a red color. **Cerous Chloride** is turned yellow.

OXALIC ACID, $H_2C_2O_4$

Occurrence and Preparation. — Oxalic acid occurs, in the form of its acid potassium and calcium salts, in the sap of many plants.

It is prepared in large amounts by heating sawdust with molten caustic alkali. The resulting potassium salt is precipitated with milk of lime, forming the insoluble calcium salt; and the latter is decomposed with sulfuric acid. Oxalic acid is also formed by the oxidation of innumerable organic substances such as sugar, starch, and cellulose (paper), by means of concentrated nitric acid.

It crystallizes from aqueous solutions in the form of colorless monoclinic prisms, $H_2C_2O_4 \cdot 2\,H_2O$. The crystallized, hydrated acid is soluble in water, alcohol, or ether: 100 parts water at 20° dissolve 11.1 parts oxalic acid; 100 parts alcohol at 15° dissolve 33.2 parts oxalic acid; 100 parts ether at 15° dissolve 1.5 parts oxalic acid.

By allowing the hydrated acid to stand over sulfuric acid, water is lost, and the anhydrous acid remains, which, when heated to about 150° C sublimes, forming needles. If heated still higher it is completely decomposed into water, carbon dioxide, and carbon monoxide:

$$H_2C_2O_4 \rightarrow H_2O + CO_2\uparrow + CO\uparrow$$

Properties. — Oxalic acid is a fairly strong, dibasic acid, and forms neutral and acid salts, *e.g.*, potassium oxalate, $K_2C_2O_4$; potassium binoxalate, KHC_2O_4; potassium tetroxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2\,H_2O$.

Solubility. — The oxalates are mostly insoluble in water, with the exception of the oxalates of the alkalies and of magnesium. In an excess of an alkali oxalate many of the insoluble oxalates dissolve. Thus ink spots and rust spots can often be removed from clothing by means of a solution of oxalic acid or of potassium tetroxalate:

$$Fe_2O_3 + 6\,H_2C_2O_4 \rightarrow 2\,H_3[Fe(C_2O_4)_3] + 3\,H_2O$$

Oxalic acid is also a good solvent for ferric phosphate. All oxalates dissolve readily in mineral acids.

Reactions in the Wet Way

A solution of ammonium oxalate can be used for the following reactions:

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid,** on warming, acts as a dehydrating agent, causing the evolution of equal volumes of carbon monoxide and carbon dioxide; the former will burn with a blue flame:

$$H_2C_2O_4 \rightarrow H_2O + CO\uparrow + CO_2\uparrow$$

3. **Silver Nitrate** precipitates white, curdy silver oxalate,

$$C_2O_4^{--} + 2\,Ag^+ \rightarrow Ag_2C_2O_4$$

almost insoluble in water, but readily soluble in ammonia and in nitric acid.

4. **Barium Chloride** precipitates white barium oxalate, soluble in oxalic and acetic acids.

5. **Calcium Chloride** precipitates white calcium oxalate, insoluble in oxalic acid, ammonium oxalate, and acetic acid, but readily soluble in hydrochloric and nitric acids. It is the most insoluble of all oxalates, and a precipitate is obtained when **calcium sulfate** is added to a solution of oxalate which is acid with acetic acid.

6. **Ferrous Phosphate** in phosphoric acid solution gives a dark yellow color with a warm solution of an oxalate.

7. **Lead Salts** precipitate white lead oxalate, soluble in nitric acid.

8. **Manganese Dioxide** mixed with oxalic acid or an oxalate, heated with water and a few drops of concentrated sulfuric acid causes decomposition of the oxalate and vigorous evolution of carbon dioxide:

$$\mathbf{MnO_2} + H_2C_2O_4 + H_2SO_4 \rightarrow MnSO_4 + 2\,CO_2\uparrow + 2\,H_2O$$

Similarly, if oxalic acid or an oxalate is added to a hot acid solution of permanganate, the oxalate is oxidized to carbon dioxide and the permanganate ion is decolorized:

$$2\,MnO_4^- + 5\,C_2O_4^{--} + 16\,H^+ \rightarrow 2\,Mn^{++} + 10\,CO_2\uparrow + 8\,H_2O$$

9. **Manganous Sulfate** or **Chloride** precipitates nearly white crystals of manganous oxalate:

$$Mn^{++} + C_2O_4^{--} + 3\,H_2O \rightarrow \mathbf{MnC_2O_4 \cdot 3\,H_2O}$$

10. **Manganous Sulfate.** — A sensitive test for the detection of oxalic acid in the presence of hydrochloric, sulfuric, nitric, phosphoric, acetic, butyric, valeric, citric, tartaric, benzoic, and salicylic acid as well as phenol or small quantities of formic acid is performed as follows:

Dissolve a small crystal (3 to 5 mg) of manganous sulfate in a few drops of water, add a drop of sodium hydroxide solution, heat somewhat, then cool and add drop by drop the solution of oxalic acid or of oxalate, which is slightly acid with sulfuric acid and free from reducing agents. The precipitate of manganous-manganic hydroxide, which was formed by the action of the sodium hydroxide on the manganese sulfate, dissolves by the action of the oxalic acid, and a red coloration is obtained, which is probably due to the formation of $[Mn(C_2O_4)_3]^{---}$.

11. **Resorcinol,** $C_6H_4(OH)_2$, dissolved in about 100 times its weight of concentrated sulfuric acid, gives a blue coloration when added to a solid oxalate and heated until fumes of sulfuric acid are evolved.

Analysis of Oxalates

Oxalates of alkaline earth metals undergo metathesis when boiled with a concentrated solution of **sodium carbonate.** Insoluble alkaline earth carbonate and soluble sodium oxalate are formed, and, after filtering, the solution can be tested

for oxalate. Such a metathesis does not always succeed with oxalates of some other metals, because, owing to the formation of complex salts, the precipitation of the carbonate is often incomplete; thus nickel oxalate forms a soluble sodium nickel oxalate. In such cases, in order to obtain an aqueous oxalic acid solution from an insoluble oxalate, and to remove the cation which may interfere in the tests, it is best to place a little of the powder in warm water and saturate with hydrogen sulfide; the less soluble nickel sulfide is formed and the solution contains oxalic acid and hydrogen sulfide:

$$NiC_2O_4 + H_2S \rightarrow NiS + H_2C_2O_4$$

Behavior of Oxalates on Ignition

All oxalates are decomposed on ignition with slight carbonization. The oxalates of the alkalies and alkaline earths are changed to carbonates, with evolution of carbon monoxide. Stronger ignition causes the formation of more or less oxide, the alkaline earth carbonate being quantitatively changed to oxide by heating over the blast lamp. The oxalates of the noble metals, and of iron, nickel, cobalt, copper, etc., leave the metal itself; the oxide is formed in the case of other metals.

TARTARIC ACID, $H_2C_4H_4O_6$

Occurrence. — Tartaric acid occurs partly free and partly as its acid potassium salt in many fruit saps, particularly in that of the grape.

Properties. — The free acid crystallizes in clear, monoclinic prisms, without water of crystallization.

Inspection of the structural formula of tartaric acid

$$\begin{array}{l} HO - CH - COOH \\ \quad\quad\quad | \\ HO - CH - COOH \end{array}$$

shows that there are in the molecule two carbon atoms each of which has the four valences satisfied by unlike atoms or groups of atoms. Thus each of these carbon atoms has one valence bond satisfied by H, one by OH, one by COOH, and one by CH(OH)COOH. Such an atom of carbon is called an *asymmetric carbon* atom, and whenever it occurs there usually exist so-called *stereoisomeric* compounds, *i.e.*, compounds which have the same chemical composition but differ in the way the atoms are arranged around the asymmetric carbon atom.

Isomeric compounds of this nature usually show practically the same chemical properties but can be distinguished physically from one another by the shape of the crystals and by the way in which the plane of polarized light is changed when passed through a solution of the crystals.

On account of the two asymmetric carbon atoms in the tartaric acid molecule, four modifications of this acid exist, and the study of these acids has played an important part in the development of chemical theory. One of these has the atoms arranged around each asymmetric carbon atom in such a way that each causes the plane of polarized light to rotate to the right. This acid, the ordinary tartaric acid, is called *d*-tartaric acid. Another acid has the atoms arranged so that just the opposite effect upon polarized light is produced; it is called *l*-tartaric acid. Crystals of these substances are to one another as mirror images, or as the right glove to the left; both form similar hemihedral crystals but certain surfaces found on the right in one case occur on the left in the other.

The third isomeric modification is that known as *d*, *l*-tartaric acid and is called *racemic acid*. It consists of an equal quantity of both of the above two acids and is optically inactive. Finally, the fourth isomer is called *mesotartaric acid* and is optically inactive because the two asymmetric carbon atoms have the groups around them arranged so that one neutralizes the other in the molecule.

Tartaric acid is very readily soluble in water (100 parts water dissolve 132 parts of tartaric acid at 15°) and alcohol, but it is insoluble in ether. It is a fairly strong acid, the ionization constant for the primary ionization being 0.97×10^{-3}, at 25°. The salts are called tartrates.

Solubility. — The neutral alkali tartrates are very soluble in water, as also is sodium acid tartrate, while the potassium acid and the ammonium acid tartrates are difficultly soluble in water.

The remaining tartrates are difficultly soluble in water, but all dissolve, more or less readily, in neutral alkali tartrate solution, forming complex salts. These com-

plex salts often conceal the reactions which are typical of the metal ions contained in them. Thus ammonium hydroxide causes no precipitation in solutions of iron, aluminum, titanium, chromium, antimony, and tin tartrates. Complex tartrate ions are also formed with manganese, cobalt, nickel, lead, copper, boron, molybdenum, and other elements.

The most important commercial salts of this acid are "cream of tartar," $KHC_4H_4O_6$; "Rochelle salt," $KNaC_4H_4O_6$; and "tartar emetic," $K(SbO)C_4H_4O_6$.

Reactions in the Wet Way

A solution of Rochelle salt (sodium potassium tartrate) may be used for these reactions.

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid** causes carbonization on warming, with evolution of sulfur dioxide, carbon monoxide, carbon dioxide, and other gases. The sulfuric acid becomes brown, and there is an empyreumatic odor.

3. **Silver Nitrate** produces no precipitation in a solution of free tartaric acid, but in the solution of a neutral tartrate, a white, curdy precipitate is formed immediately:

$$C_4H_4O_6^{--} + 2\,Ag^+ \rightarrow Ag_2C_4H_4O_6$$

The precipitate is soluble in nitric acid and in ammonia. By warming the ammoniacal silver tartrate solution, metallic silver is deposited. This very important reaction for the detection of tartaric acid is performed in the following manner:

Treat the pure tartrate solution with silver nitrate solution until no further precipitation takes place; add a few drops of sodium hydroxide solution and dilute ammonia drop by drop until the precipitate just dissolves. Place the test tube containing the solution in water which has been heated to 60–70° C. After standing for about fifteen minutes, the silver will be deposited in the form of a beautiful mirror on the sides of the test tube. This very delicate reaction cannot be performed with certainty in the presence of other acids. In this case the tartaric acid should first be precipitated as potassium acid tartrate. Concentrate the solution to a small volume, add a little solid potassium carbonate, acidify with strong acetic acid and stir the cold solution vigorously; a precipitate of potassium acid tartrate will form at once if considerable tartrate is present. Filter off the precipitate, wash with a little cold water, and dissolve it in as little caustic soda solution as possible. In this way a solution is obtained which will readily give the silver mirror on the addition of silver nitrate and treatment as above.

If no precipitate is formed on the addition of the acetic acid, add a little alcohol, which causes the precipitate to form more readily. Filter off the precipitate, wash with diluted alcohol, dry, dissolve in dilute sodium hydroxide, and treat as above. If the alcohol is not removed by drying, a mirror is sometimes formed when tartaric acid is absent.

4. **Ammonium Molybdate** in faintly acid solutions together with a little tartaric acid and one or two drops of hydrogen peroxide, in a solution heated to about 60°, gives a coloration at first pale yellow, then green, and finally blue.

5. **Calcium Chloride.** — If to a concentrated solution of neutral alkali tartrate, in the absence of ammonium salts, calcium chloride solution is added drop by drop, a white amorphous precipitate is formed which redissolves, forming soluble calcium tartrate anions:

$$2\ C_4H_4O_6^{--} + Ca^{++} \rightarrow [Ca(C_4H_4O_6)_2]^{--}$$

Only after the addition of enough calcium chloride to decompose completely the alkali tartrate is a permanent precipitate formed, which at first is flocculent, but soon becomes crystalline, consisting of neutral calcium tartrate:

$$[Ca(C_4H_4O_6)_2]^{--} + Ca^{++} \rightarrow 2\ CaC_4H_4O_6$$

In dilute solutions the first addition of calcium chloride often produces no precipitation; but after standing some time (or more quickly on rubbing the sides of the test tube with a glass rod) the crystalline precipitate is deposited, $CaC_4H_4O_6 + 4\ H_2O$. Calcium tartrate is difficultly soluble in water; 100 parts of water at 15° C dissolve 0.0159 part of the crystalline salt, and 100 parts of boiling water dissolve 0.0285 part of the salt. The precipitate is soluble in acetic acid (difference from calcium oxalate) and also in a solution of concentrated caustic alkali (free from carbonate), probably forming a complex ion:

$$2\ CaC_4H_4O_6 + 2\ OH^- \rightarrow H_2O + [(CaC_4H_4O_6)_2O]^{--}$$

On boiling this solution, calcium tartrate is reprecipitated in the form of a voluminous gelatinous precipitate, which again goes into solution on cooling. The presence of ammonium chloride retards the formation of the calcium tartrate, but does not prevent it; after standing some time the precipitate settles out in the form of a heavy crystalline powder (difference from citric acid).

The calcium salt of *d*, *l*-tartaric acid is less soluble than calcium *d*-tartrate and has a silky luster. The presence of aluminum, ferric, or antimonyl ions tends to prevent the formation of calcium tartrate on account of the formation of complex ions.

6. **Ferrous Salt** added in small quantity to free tartaric acid or an alkali tartrate gives, with two drops of hydrogen peroxide or a few grains of sodium peroxide, a beautiful violet coloration. The sensitive reaction is not obtained with citric, malic, or succinic acids.

7. **Lead Acetate** produces in neutral solutions a white, flocculent precipitate of lead tartrate, easily soluble in nitric acid and in ammonia.

8. **Magnesium Chloride Reagent.** — If a concentrated tartaric acid solution is treated with an excess of magnesium chloride, 10 ml of strong ammonia, and a volume of alcohol equal to that of the solution, then, after shaking and allowing to stand twelve hours, the tartaric acid is precipitated quantitatively as crystalline, basic magnesium tartrate

insoluble in 50 per cent alcohol (difference from malic and succinic acids):

$$C_4H_4O_6^{--} + 2\,Mg^{++} + 2\,OH^- + H_2O \rightarrow \mathbf{Mg_2(OH)_2(C_4H_4O_6) \cdot H_2O}$$

Filter off the precipitate obtained in the above test, wash it with 50 per cent alcohol, dry, and transfer the precipitate to a test tube, with the aid of a glass rod. Add a little silver nitrate solution and a slight excess of 6-normal ammonium hydroxide, and heat to about 60°. A mirror should form if a tartrate is present.

9. **Potassium Chromate** solution poured over a crystal of tartaric acid at room temperature gives a purple-violet or black coloration and evolution of carbon dioxide. Citric acid crystals, when tested the same way, give a coffee-brown color. In aqueous solution, tartaric acid will give the test: add a little dilute sulfuric acid to the aqueous tartrate solution and one or two drops of potassium chromate or dichromate solution and heat for some time; the yellow color of the chromate changes gradually to bluish violet.

10. **Potassium Salts** produce no precipitation in neutral solutions of alkali tartrates; but if the concentrated solution is acidified with acetic acid, a crystalline precipitate of potassium acid tartrate is formed upon stirring vigorously:

$$C_4H_4O_6^{--} + K^+ + H^+ \rightarrow \mathbf{KHC_4H_4O_6}$$

Potassium acid tartrate is difficultly soluble in water (100 ml of water dissolves 0.45 g of salt) and in acetic acid, but is readily soluble in mineral acids or in caustic alkali and alkali carbonate solutions. The precipitate may be dissolved in a little ammonia and the test with calcium chloride obtained (p. 384).

If a concentrated solution of free tartaric acid is treated with potassium chloride, a precipitate of potassium acid tartrate is formed in spite of the presence of the hydrochloric acid which is set free. From dilute solutions the precipitate appears only after adding sodium acetate (cf. p. 283).

The presence of considerable boric acid greatly interferes with the formation of the potassium acid tartrate. In such cases add ammonium chloride to the concentrated solution in a test tube, then some calcium chloride solution, and rub the inside walls of the tube with a stirring rod. If only a little tartaric acid is present it may be necessary to let the solution stand twenty-four hours. Filter off any precipitate that may form, wash it two or three times with alcohol, and dissolve the calcium tartrate in a little freshly prepared potassium hydroxide solution (1 : 5). Filter and heat the filtrate to boiling. Amorphous calcium tartrate should be precipitated. Another way to identify the tartrate in the first precipitate of calcium tartrate is as follows: Place the washed precipitate in a test tube, add a crystal of silver nitrate and a few drops of 6-normal ammonium hydroxide, and place the test tube in hot water; a distinct silver mirror should form if a tartrate is present.

11. **Resorcinol** in concentrated sulfuric acid (1 : 100) gives a wine-red color when heated with a little solid tartaric acid, or a tartrate, until sulfuric acid fumes are evolved. A mere trace of tartaric acid will give the reaction, but nitrates, nitrites, chlorates, and other oxidizing agents interfere.

Reactions in the Dry Way

If tartaric acid is heated to 135° C, it melts, and on stronger ignition it is decomposed, leaving a residue of carbon and giving off gases with an odor resembling that of burnt sugar.

The alkali tartrates are also decomposed by ignition, leaving a residue of carbon and alkali carbonate, which effervesces on treatment with acid.

Ammonium tartrate leaves a residue of carbon, which does not effervesce on treatment with acids. The tartrates of the alkaline earths leave behind a mixture of carbon and carbonate; on very strong ignition the latter is changed to oxide.

The tartrates of those metals whose oxides are reduced by carbon are left in the form of metal (Ag, Pb, Fe, Ni, Co, etc.).

CITRIC ACID, $H_3C_6H_5O_7$

Occurrence and Properties. — Citric acid is found in nature in the juices of many fruits. It is a tribasic acid, readily soluble in water and in alcohol, but difficultly soluble in ether. The pure acid is a colorless, odorless solid which usually contains three molecules of water of crystallization, $H_3C_6H_5O_7 \cdot 3\ H_2O$. Heated carefully to 55° it loses its water of crystallization and at a higher temperature melts and begins to decompose, giving rise to acrid vapors and an odor similar to that obtained with tartaric acid under similar treatment. The aqueous solution is optically inactive and shows fairly strong acid properties, the constant for the primary ionization being 0.82×10^{-3} at 25°. The clear transparent crystals weather on standing in the air owing to loss of water of crystallization; the crystals become opaque and powdery. Its salts are called citrates.

Solubility. — The citrates of the alkalies are soluble in water, and form, with the insoluble citrates of the heavy metals, very soluble complex salts, whose solutions are not precipitated by alkali hydroxides, alkali carbonates, ammonia, etc.

Reactions in the Wet Way

A solution of potassium citrate may be used.

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid** on being heated with a citrate, as with most α-hydroxyacids, causes formic acid, HCO_2H, to be formed, which then breaks down into water and CO; at the same time some acetonedicarboxylic acid, $(CH_2)_2CO \cdot (CO_2H)_2$, is formed, and this breaks down into acetone, $(CH_3)_2CO$, and CO_2.

$$H_3C_6H_5O_7 \rightarrow HCO_2H + (CH_2)_2CO \cdot (CO_2H)_2$$

$$HCO_2H \rightarrow H_2O + CO,\ (CH_2)_2CO \cdot (CO_2H)_2 \rightarrow (CH_3)_2CO + 2\ CO_2\uparrow$$

A part of the citric acid is carbonized, and this causes reduction of the sulfuric acid so that some SO_2 is evolved.

3. **Silver Nitrate** produces in neutral solutions a flocculent precipitate of silver citrate, $Ag_3C_6H_5O_7$, readily soluble in nitric acid and in ammonia. On heating the ammoniacal solution to 60° C, no silver mirror is formed; but on heating the solution to boiling, the silver is gradually deposited.

4. **Barium** or **Calcium Chloride** gives no precipitation in neutral solutions (difference from tartaric acid). If, however, caustic soda solution is added to the solution which contains an excess of calcium chloride, a flocculent precipitate of tertiary calcium citrate is at once formed, insoluble in caustic alkali, but readily soluble in ammonium chloride. On boiling the solution in ammonium chloride, crystalline

calcium citrate is precipitated, which is now insoluble in ammonium chloride.

5. **Lime Water** in excess produces no precipitation in cold solutions of neutral citrates; on boiling, there is formed a flocculent precipitate of calcium citrate, which almost entirely redissolves on cooling.

6. **Lead Acetate** precipitates from solutions of the free acid, and those containing neutral salts, amorphous $Pb_3(C_6H_5O_7)_2 \cdot H_2O$.

7. **L. Stahre's Test for Citric Acid.*** — To the solution of free citric acid in water, or to the solution of a citrate in very dilute sulfuric or nitric acid (not hydrochloric) add 2 to 5 drops of tenth-normal permanganate solution and heat a short time at 30° to 40° (the solution must not boil!). As soon as the solution is colored brown, or becomes turbid by the precipitation of a little manganese dioxide, add 1 or 2 drops of ammonium oxalate solution and about 1 ml of 10 per cent sulfuric acid, which will clear up the solution. Now, add a few drops of bromine water, and a distinct, crystalline precipitate of pentabromacetone will be obtained. The bromine water may also be added before the permanganate solution and sometimes the results are better.

This test is so sensitive that 0.3 mg of citric acid in 1 ml of water can be detected.

The experiment succeeds in the presence of tartaric, malic, oxalic, sulfuric, and phosphoric acids, except that a little more permanganate is required.

In the Stahre test the following reactions take place:

(*a*) The permanganate oxidizes the citric acid to acetonedicarboxylic acid with evolution of carbon dioxide:

$$5\,H_3C_6H_5O_7 + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,CO_2 + 2\,Mn^{++} + 8\,H_2O + 5\,(CH_2)_2CO(CO_2H)_2$$

(*b*) The acetonedicarboxylic acid reacts with bromine, forming pentabromacetone:

$$(CH_2)_2CO(CO_2H)_2 + 5\,Br_2 \rightarrow 2\,CO_2 + 5\,HBr + C_2HBr_5CO$$

If the permanganate is allowed to act longer upon the citric acid the acetonedicarboxylic acid is converted gradually into acetone, the reaction taking place more quickly on boiling:

$$(CH_2)_2CO(CO_2H)_2 \rightarrow 2\,CO_2 + (CH_3)_2CO$$

Acetone itself is not brominated as readily as the acetonedicarboxylic acid, and for this reason care should be taken not to let the temperature rise above 40° during the treatment of the citric acid with permanganate.

The citrates on treatment with bromine, without previous oxidation with permanganate, will also give pentabromacetone:

$$K_3C_6H_5O_7 + 6\,Br_2 \rightarrow 3\,KBr + 3\,CO_2 + 4\,HBr + C_2HBr_5CO$$

8. **Mercuric Sulfate.** — Denigès' reagent.† Dissolve 5 g HgO in 100 ml of water and 20 ml concentrated H_2SO_4. Treat the solution of the citrate with 1/20 as much reagent and heat to boiling, then add a few drops of 0.1 *N* $KMnO_4$ solution. A white crystalline precipitate is formed.

The precipitate has the composition: $Hg_3O_2SO_4 \cdot 2[CO(CH_2CO_2)_2]Hg$ and is a mixture of basic mercuric sulfate and the mercuric salt of acetonedicarboxylic

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* L. Stahre, *Z. anal. Chem.*, **36**, 195 (1897); also Alfred Wöhlk, *ibid.*, **41**, 94 (1902).

† *Compt. rend.*, **138**, 32; *Z. anal. Chem.*, **38**, 718 (1899); and **40**, 121 (1901).

acid. The reaction is very sensitive and enables one to detect 0.5 g of citric acid dissolved in a liter of water. The reaction, however, is not peculiar to citric acid but is shown by many other ketonic compounds.

9. Citric acid may be distinguished from oxalic, tartaric, and malic acid by means of the deep blue or green color obtained by the following treatment:

To at least 0.01 g of citric acid add an excess of ammonium hydroxide (3 ml) in a piece of ignition tubing closed at one end. Seal the other end of the tubing so that but little empty space is above the liquid and heat 6 hours at 110° to 120°. Cool, break off the end of the tubing, and pour the liquid into a shallow porcelain dish. After standing several hours in the light a blue or green product is obtained.

This characteristic coloration may also be obtained as follows: To the citric acid add a little glycerol (a little less than the quantity of citric acid used) and heat gently until the mass begins to swell. Dissolve the residue in ammonia, evaporate off most of the liquid, and add a little water and 2 drops of fuming nitric acid which has been diluted with five times as much water. The green color which appears first changes by heating on the water-bath to blue. Hydrogen peroxide can be used in place of the nitric acid.

Reactions in the Dry Way

The citrates, on ignition, behave exactly like the tartrates.

PHOSPHOROUS ACID, H_3PO_3

Formation. — By the slow combustion of phosphorus in the air phosphorus trioxide is formed which, since it is the anhydride of phosphorous acid, reacts with cold water to form the acid:

$$P_2O_3 + 3\ H_2O \rightarrow 2\ H_3PO_3$$

Phosphorous acid is formed much more readily by the action of water on the trihalides of phosphorus:

$$PCl_3 + 3\ HOH \rightarrow 3\ HCl + H_3PO_3$$

The hydrochloric acid is removed by evaporation, and the last traces of uncombined water by heating to 180°. If the mass is then allowed to cool, it solidifies to a crystalline, hygroscopic substance which melts at −73.6°.

By neutralizing the solution of phosphorous acid with bases, the phosphites are obtained. It is never possible, however, to replace more than two of the hydrogen atoms with metal so that phosphorous acid is considered to be a dibasic acid. Certain organic compounds are known, however, which are derived from tribasic phosphorous acid, H_3PO_3. Phosphorous acid is a strong reducing agent and changes to phosphoric acid by merely standing in the air.

Solubility. — Only the phosphites of the alkalies are soluble in water, but all are soluble in acid.

Reactions in the Wet Way

A solution of sodium phosphite should be used.

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid** causes no reaction in the cold; on heating, the phosphorous acid reduces the sulfuric acid to sulfurous acid, easily recognized by the odor:

$$H_3PO_3 + H_2SO_4 \rightarrow H_3PO_4 + H_2O + SO_2\uparrow$$

3. **Silver Nitrate** produces at first a white precipitate of silver phosphite,

$$HPO_3^{--} + 2\ Ag^+ \rightarrow \mathbf{Ag_2HPO_3}$$

which in a concentrated solution is changed in the cold to metallic silver; in dilute solutions this reduction takes place only on warming:

$$\mathbf{Ag_2HPO_3} + H_2O \rightarrow H_3PO_4 + 2\ Ag$$

4. **Barium Chloride** precipitates white barium phosphite, soluble in all acids.

5. **Ammonium Molybdate** gives in hot solution a yellow, crystalline precipitate of $(NH_4)_2HPO_3 \cdot 6\ MoO_3 \cdot 2\ H_2O$.

6. **Lead Acetate** precipitates white lead phosphite, insoluble in acetic acid.

7. **Mercuric Chloride** is slowly reduced by phosphorous acid in the cold, but more quickly on warming, to mercurous chloride:

$$2\ HgCl_2 + H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2\ HCl + \mathbf{Hg_2Cl_2}$$

If the phosphorous acid is present in excess, the reduction in the hot solution (not in the cold) goes farther, and gray metallic mercury is deposited:

$$\mathbf{Hg_2Cl_2} + H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2\ HCl + 2\ \mathbf{Hg}$$

Mercurous Nitrate is reduced to mercury under the same conditions.

8. Concentrated **Potassium Hydroxide Solution** changes a phosphite to phosphate, with evolution of hydrogen,

$$K_2HPO_3 + KOH \rightarrow K_3PO_4 + H_2\uparrow$$

but with dilute caustic potash the hydrogen evolution is very slight.

9. **Sulfurous Acid** is reduced by phosphorous acid to hydrogen sulfide:

$$3\ H_3PO_3 + H_2SO_3 \rightarrow 3\ H_3PO_4 + H_2S\uparrow$$

Sulfur Dioxide in a boiling solution containing phosphite gives sulfur and phosphate:

$$SO_2 + 2\ HPO_3^{--} \rightarrow \mathbf{S} + 2\ HPO_4^{--}$$

10. **Zinc** in sulfuric acid solution reduces phosphorous acid to phosphine:

$$H_3PO_3 + 3\ \mathbf{Zn} + 6\ H^+ \rightarrow 3\ Zn^{++} + 3\ H_2O + PH_3\uparrow$$

If the phosphine is allowed to act upon a concentrated solution of silver nitrate (1 : 1), or, better still, upon solid silver nitrate, the latter is colored yellow, as with arsine:

$$PH_3 + 6\ AgNO_3 \rightarrow \mathbf{PAg_3 \cdot 3\ AgNO_3} + 3\ HNO_3$$

By the addition of water this yellow compound is decomposed with separation of grayish white silver:

$$\mathbf{PAg_3 \cdot 3\ AgNO_3} + 3\ H_2O \rightarrow 3\ HNO_3 + H_3PO_3 + 6\ \mathbf{Ag}$$

The phosphorous acid is, however, immediately oxidized by the nitric acid to phosphoric acid:

$$3\ H_3PO_3 + 2\ HNO_3 \rightarrow H_2O + 2\ NO + 3\ H_3PO_4$$

A mixture of phosphine and hydrogen burns with an emerald-green flame.

Reactions in the Dry Way

By ignition, phosphorous acid (like hypochlorous acid) is changed at the cost of its own oxygen to the higher compound, while the oxidizing

part of the acid is reduced to its hydrogen compound:

$$3\ HClO \rightarrow HClO_3 + 2\ HCl$$

$$4\ H_3PO_3 \rightarrow 3\ H_3PO_4 + PH_3\uparrow$$

The phosphites behave similarly:

$$8\ Na_2HPO_3 \rightarrow 4\ Na_3PO_4 + Na_4P_2O_7 + H_2O + 2\ PH_3\uparrow$$

METAPHOSPHORIC ACID, HPO_3

Preparation and Properties. — The monobasic metaphosphoric acid is obtained by treating phosphorus pentoxide with cold water,

$$P_2O_5 + H_2O \rightarrow 2\ HPO_3$$

and also by the strong ignition of orthophosphoric acid:

$$H_3PO_4 \rightarrow H_2O + HPO_3$$

Metaphosphoric acid is a colorless, glassy, hygroscopic mass. On boiling its aqueous solution, or slowly in the cold, it takes up water, and is changed to orthophosphoric acid:

$$HPO_3 + H_2O \rightarrow H_3PO_4$$

The metaphosphates are readily obtained by heating the monometallic salts of orthophosphoric acid,

$$NaH_2PO_4 \rightarrow H_2O + NaPO_3$$

or by igniting sodium ammonium phosphate:

$$NaNH_4HPO_4 \rightarrow H_2O + NH_3 + NaPO_3$$

The meta-salts are changed into orthophosphates by boiling the aqueous solution in the presence of mineral acid.

There are at least eight different varieties of metaphosphates corresponding to the general formula $(MPO_3)_n$ in which M is a univalent metal. Most of these have been found to give corresponding polymeric free acids of the type $(HPO_3)_n$. Some of the sodium metaphosphates are soluble in water and some are not. A soluble form of $(NaPO_3)_6$ is now coming into use as a cleaning agent and water softener. The commercial preparation *Calgon* contains such a product.

Solubility. — The metaphosphates of the alkalies and of magnesium are soluble in water; the remaining salts are difficultly soluble or insoluble in water, readily soluble in nitric acid and in an excess of metaphosphoric acid or an excess of alkali metaphosphate.

Reactions in the Wet Way

Sodium metaphosphate is used for the following tests:

1. **Sulfuric Acid** causes no visible reaction.

2. **Silver Nitrate** precipitates white silver metaphosphate, soluble in ammonia and in nitric acid:

$$PO_3^- + Ag^+ \rightarrow \mathbf{AgPO_3}$$

3. **Barium Chloride** precipitates voluminous barium metaphosphate, soluble in an excess of sodium metaphosphate, from which solution ammonia causes no precipitation. Barium sodium dimetaphosphate (or a similar polymetaphosphate) is probably formed.

4. **Albumin Solution** is coagulated by an aqueous solution of the free acid (difference from pyro- and orthophosphoric acids), but not by a solution of alkali metaphosphate, except on the addition of acetic acid.

5. **Ammonium Molybdate** produces no precipitate in the cold; but, on boiling the acid solution, metaphosphoric acid is changed to orthophosphoric acid and the characteristic precipitate of ammonium phosphomolybdate is formed.

6. **Magnesium Salts** cause no precipitate from moderately dilute solutions, even on boiling (difference from orthophosphoric acid).

7. **Zinc in Acid Solution** does not reduce metaphosphoric acid (difference from phosphorous acid).

Behavior of Metaphosphates on Ignition

The alkali metaphosphates, on being fused, form a glassy mass, which has the property of dissolving many metallic oxides, forming orthophosphates with characteristic colors. (See Phosphoric Acid.) By fusion with soda, orthophosphates are formed from metaphosphates.

PYROPHOSPHORIC ACID, $H_4P_2O_7$

Preparation and Properties. — The tetrabasic pyrophosphoric acid is formed by heating orthophosphoric acid to 213°. It is a soft, glassy mass, readily soluble in water; in aqueous solution it gradually adds water to the molecule and is changed to phosphoric acid, the change taking place quickly on boiling the solution.

The salts of pyrophosphoric acid, the pyrophosphates, are obtained by igniting the dimetallic phosphates:

$$2\ Na_2HPO_4 \rightarrow H_2O + Na_4P_2O_7$$

Solubility. — The pyrophosphates of the alkalies are soluble in water; the remaining pyrophosphates are difficultly soluble or insoluble in water, but all are soluble in acids, and some are soluble in an excess of sodium pyrophosphate.

Reactions in the Wet Way

A solution of sodium pyrophosphate is used for these tests.

1. **Sulfuric Acid.** — No reaction.
2. **Silver Nitrate** gives a white, curdy precipitate, soluble in ammonia and in nitric acid.
3. **Barium Chloride** causes a white, amorphous precipitate, soluble in acids.
4. **Albumin** is not coagulated by free pyrophosphoric acid (difference from metaphosphoric acid).
5. **Ammonium Molybdate** produces no precipitation in the cold; but, on warming, yellow ammonium phosphomolybdate is precipitated.
6. **Cadmium Chloride** gives a white precipitate in acetic acid solutions. Ortho- and metaphosphates do not give these last two reactions.
7. **Cupric Sulfate** gives a pale blue precipitate.
8. **Magnesium Chloride** produces a white precipitate which is soluble in an excess of the magnesium salt, as well as in an excess of sodium pyrophosphate. By boiling this solution a precipitate is formed, which does not disappear on cooling.

Reactions in the Dry Way

All pyrophosphates on being fused with sodium carbonate are changed to orthophosphates:

$$Na_4P_2O_7 + Na_2CO_3 \rightarrow CO_2 + 2\ Na_3PO_4$$

Iodic Acid, HIO_3

Occurrence. — In sea-water and in Chile saltpeter as potassium iodate.

Formation. — By oxidizing iodine with fuming nitric acid or by the action of chlorine upon iodine suspended in water:

$$3\ I_2 + 10\ HNO_3 \rightarrow 6\ HIO_3 + 10\ NO\uparrow + 2\ H_2O$$

$$I_2 + 6\ H_2O + 5\ Cl_2 \rightarrow 10\ HCl + 2\ HIO_3$$

Properties. — Iodic acid itself is a colorless solid which crystallizes in the orthorhombic system. Its anhydride, I_2O_5, is obtained as a white crystalline powder. Both dissolve in water and on being heated give iodine, oxygen, and water as decomposition products. Iodic acid is a strong acid and its solutions are largely ionized.

The most important iodate, KIO_3, is obtained by the action of iodine upon a slightly acid solution of potassium chlorate:

$$5\ KClO_3 + 3\ I_2 + 3\ H_2O \rightarrow 5\ KIO_3 + HIO_3 + 5\ HCl$$

Iodates are also formed by the action of iodine upon alkali hydroxide solutions:

$$3\ I_2 + 6\ KOH \rightarrow 5\ KI + KIO_3 + 3\ H_2O$$

In alkaline solutions iodides are oxidized to iodates by hypochlorites and potassium permanganate.

Solubility. — The iodates of the alkalies are soluble in water, but the remaining iodates are difficultly soluble or insoluble.

Reactions in the Wet Way

1. **Sulfuric Acid.** — Neither dilute nor concentrated sulfuric acid decomposes iodic acid; but if reducing substances are present at the same time (such as hydriodic acid, hydrogen sulfide, ferrous salts, etc.), the iodic acid is reduced, with separation of iodine:

$$IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ H_2O + 3\ I_2$$

2. **Silver Nitrate** precipitates white, curdy silver iodate, $AgIO_3$, readily soluble in ammonia, but difficultly soluble in nitric acid.

3. **Barium Chloride** precipitates white barium iodate, difficultly soluble in hot water (100 parts of boiling water dissolve 0.6 part of the salt), and only slowly soluble in dilute hydrochloric or nitric acids.

4. **Lead Acetate** precipitates lead iodate, difficultly soluble in water and only slightly soluble in nitric acid.

5. **Reducing Agents.**

(*a*) *Hydriodic acid* reduces iodic acid, with separation of iodine:

$$IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ H_2O + 3\ I_2$$

The presence of acid is necessary and the reaction will continue only as long as an appreciable quantity of hydrogen ions is present. Iodide and iodate ions, therefore, cause neutralization of a solution.

If the solution is concentrated, the iodine separates out as a brown powder; dilute solutions are colored yellow. The iodine may be absorbed, with a reddish violet color, by shaking the aqueous solution with chloroform or carbon disulfide.

(*b*) *Sulfurous acid* also causes separation of iodine, unless a large excess of sulfurous acid is added:

$$2\ IO_3^- + 5\ SO_3^{--} + 2\ H^+ \rightarrow 5\ SO_4^{--} + H_2O + I_2$$
$$IO_3^- + 3\ SO_3^{--} \rightarrow 3\ SO_4^{--} + I^-$$

The reduction takes place according to the last reaction when three molecules of sulfurous acid are present to one of iodate; sulfurous acid reacts with free iodine (cf. p. 367).

(*c*) *Zinc dust* (or, better, Devarda's alloy) reduces neutral iodate solutions to iodide.

(*d*) *Hydrogen sulfide* reacts with iodic acid causing precipitation of sulfur and, at first, iodine is liberated:

$$2\ IO_3^- + 5\ H_2S + 2\ H^+ \rightarrow I_2 + 5\ S + 6\ H_2O$$

but further addition of hydrogen sulfide causes the disappearance of the iodine:

$$I_2 + H_2S \rightarrow 2\ H^+ + 2\ I^- + S$$

The entire reaction, therefore, after an excess of hydrogen sulfide has been added, is

$$IO_3^- + 3\ H_2S \rightarrow I^- + 3\ H_2O + 3\ S$$

(*e*) *Phosphorus*, either white or red, reacts energetically with iodic acid even in dilute solutions:

$$P_4 + 4\ IO_3^- + 4\ H_2O \rightarrow 4\ H_2PO_4^- + 2\ I_2$$

(*f*) *Hypophosphorous acid* reduces iodic acid eventually to iodide in the cold. The reaction takes place in three stages:

$$IO_3^- + 3\ H_3PO_2 \rightarrow 3\ H_3PO_3 + I^-$$
$$5\ I^- + IO_3^- + 6\ H^+ \rightarrow 3\ H_2O + 3\ I_2$$
$$H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2\ HI$$

The first two stages take place very quickly, the third stage is a slow reaction, but so that the liberated iodine can be recognized easily and the reaction of hypophosphite and iodine can be used to detect as little as 1 γ of HIO_3.

Place a drop of the neutral solution to be tested on a spot plate and mix with 1 drop of starch solution and 2 drops of dilute hypophosphorous acid. Blue starch-iodide will be formed if an iodate is present.

Reactions in the Dry Way

Heated on charcoal the iodates deflagrate, but not so strongly as the chlorates; all are decomposed on being heated, some with and some without the separation of iodine. Thus all neutral iodates of the alkalies are easily decomposed into iodide and oxygen, while the bi-iodates set free iodine at the same time:

$$2\ KIO_3 \rightarrow 2\ KI + 3\ O_2$$

$$4\ [KIO_3 \cdot HIO_3] \rightarrow 4\ KI + 11\ O_2 + 2\ H_2O + 2\ I_2$$

GROUP IV

Silver Nitrate produces in neutral solutions a colored precipitate, soluble in nitric acid.

Barium Chloride also produces a precipitate which is soluble in nitric acid.

PHOSPHORIC ACID, H_3PO_4

Preparation and Properties. — Orthophosphoric acid is obtained by the oxidation of phosphorus by means of nitric acid, or by boiling the meta- and pyrophosphoric acids with water.

The anhydride, P_2O_5, is a white substance resembling snow in appearance. Exposed to the air it absorbs water rapidly and is, thus, one of the most efficient drying agents for gases. It is the anhydride of ortho-, meta-, and pyrophosphoric acids.

Orthophosphoric acid, H_3PO_4, forms water-clear crystals which are very hygroscopic and quickly become changed to a sirup by exposure to the air. By very strong heating in an open dish it can be volatilized, and the vapors fume in the air. There are but few acids which will not decompose or volatilize upon such strong heating.

Phosphoric acid, and by this name the ortho-acid is always meant unless the prefix meta or pyro is used, is tribasic and forms salts in which either one, two, or three hydrogen atoms are replaced by metals. Salts like NaH_2PO_4 and $Ca(H_2PO_4)_2$ are called preferably *primary* phosphates, but are usually named *dihydrogen* phosphates or *acid* phosphates. Salts like Na_2HPO_4 and $CaHPO_4$ are called *secondary* phosphates; the former is often called *disodium* phosphate and the latter is calcium hydrogen phosphate. Salts like Na_3PO_4 and $Ca_3(PO_4)_2$ are *tertiary* phosphates though usually called trisodium phosphate and tricalcium phosphate.

The first hydrogen of phosphoric acid corresponds to that of a moderately strong acid (cf. p. 16). The second hydrogen is ionized to about the same extent as the first hydrogen of carbonic acid or hydrogen sulfide; and is enough to give an acid reaction with phenolphthalein but not with methyl orange. The third hydrogen of phosphoric acid is scarcely ionized at all, or only about as much as the second hydrogen of hydrogen sulfide.

If a solution of phosphoric acid is neutralized with caustic soda with methyl orange as indicator, the end point will be reached when all the phosphoric acid is converted to primary phosphate or, in other words, when one hydrogen has been neutralized in every molecule of H_3PO_4. With phenolphthalein as an indicator, the end point will be reached when secondary sodium phosphate is formed.

An aqueous solution of primary sodium phosphate, NaH_2PO_4, is neutral to methyl orange and acid to phenolphthalein; an aqueous solution of secondary sodium phosphate is alkaline to methyl orange, and neutral to phenolphthalein. An aqueous solution of tertiary sodium phosphate is alkaline to all indicators.

A mixture of sodium hydroxide and phosphoric acid made in the proportion of one and one-half molecules of base to one molecule of acid will react acid to phenolphthalein and basic to methyl orange; moreover, it will take just as much half-

normal acid to neutralize such a solution with methyl orange as indicator as it does of half-normal alkali to neutralize the solution with phenolphthalein as indicator.

Solubility. — The phosphates of the alkalies are soluble in water, and so are the primary salts of the alkaline earths. The secondary phosphates of the alkaline earths are very difficultly soluble, while the corresponding tertiary phosphates (as well as all other phosphates) are insoluble. All phosphates dissolve in acids (cf. p. 51).

Reactions in the Wet Way

Use a solution of secondary sodium phosphate for these reactions.

1. **Sulfuric Acid,** dilute or concentrated, produces no visible change.

2. **Silver Nitrate** produces a yellow precipitate of silver phosphate (difference from meta- and pyrophosphoric acids),

$$2\ HPO_4^{--} + 3\ Ag^+ \rightarrow H_2PO_4^- + \mathbf{Ag_3PO_4}$$

readily soluble in nitric acid and in ammonia. Sometimes white Ag_2HPO_4 is formed in this test.

3. **Barium Chloride** precipitates a white, amorphous phosphate:

$$HPO_4^{--} + Ba^{++} \rightarrow \mathbf{BaHPO_4}$$

In the presence of ammonia the less soluble tertiary salt is precipitated:

$$2\ HPO_4^{--} + 3\ Ba^{++} + 2\ NH_3 \rightarrow 2\ NH_4^+ + \mathbf{Ba_3(PO_4)_2}$$

The barium phosphates (as well as those of the other alkaline earths) are easily dissolved by acids, even acetic acid (difference from aluminum and ferric phosphates). From these acid solutions, ammonia reprecipitates the phosphate.

In pure water $H_2PO_4^-$ is dissociated to about 0.1 per cent, but in the presence of acetic acid to a much less extent. $BaHPO_4$ in contact with water furnishes more HPO_4^{--} ions than does $H_2PO_4^-$ in the presence of acetic acid, therefore $BaHPO_4$ dissolves. Similarly $Ba_3(PO_4)_2$ dissolves in order to establish equilibrium between H^+ and PO_4^{---} ions. Aluminum phosphate is less soluble than barium phosphate and therefore a stronger acid is required to dissolve it.

By adding ammonia the hydrogen ions are neutralized, PO_4^{---} ions are obtained in equilibrium with NH_4^+ ions, and $Ba_3(PO_4)_2$ is reprecipitated.

4. **Albumin** is not coagulated by orthophosphoric acid.

5. **Ammonium Molybdate,** in large excess, precipitates from nitric acid solutions, in the cold on standing (more quickly on slightly warming) a yellow, crystalline precipitate of ammonium phosphomolybdate:

$$H_3PO_4 + 12\ (NH_4)_2MoO_4 + 21\ HNO_3 \rightarrow$$
$$\mathbf{(NH_4)_3PO_4 \cdot 12\ MoO_3} + 21\ NH_4NO_3 + 12\ H_2O$$

This reaction is analogous to that with arsenic acid (cf. p. 149), except that the arsenic compound is formed quickly only at the boiling temperature. The presence of ammonium nitrate greatly facilitates the formation of this precipitate.

Ammonium phosphomolybdate is readily soluble in alkalies and in ammonia,

$$(NH_4)_3PO_4 \cdot 12\,MoO_3 + 23\,OH^- \rightarrow 3\,NH_4^+ + HPO_4^{--} + 12\,MoO_4^{--} + 11\,H_2O$$

also in an excess of alkali phosphate solutions, forming compounds which contain less molybdenum. It is, therefore, always necessary to prevent the formation of such compounds by the addition of a large excess of ammonium molybdate.

6. **Ammonium Molybdate and Benzidine.** — Benzidine, $C_{12}H_8(NH_2)_2$, is not oxidized by molybdic acid or normal molybdates but it is oxidized by the complex phosphomolybdic acid and by the salts of this acid. By the oxidation of the benzidine and also by the reduction of phosphomolybdic acid, blue compounds are formed.

Place a drop of the acid solution to be tested on a piece of ashless filter paper and upon this a drop of 5 per cent ammonium molybdate in 0.3 *N* HNO_3 and a drop of 0.05 per cent benzidine in 10 per cent acetic acid. Hold over the neck of an open bottle of strong ammonia; a blue spot will appear with less than 1.5 γ of P_2O_5.

7. **Ferric Chloride.** — If a solution of sodium phosphate is treated with ferric chloride, a yellowish white precipitate of ferric phosphate is formed:

$$HPO_4^{--} + Fe^{+++} \rightleftarrows H^+ + FePO_4$$

Hydrogen ions are formed in this reaction, and, as might be expected from the mass-action principle, the precipitation of the phosphoric acid is not quantitative unless the greater part of the hydrogen ions are removed. This may be accomplished by adding ammonium acetate, for then the hydrogen ions must form non-ionized acetic acid to be in equilibrium with the acetate ions (cf. p. 49).

$$HPO_4^{--} + C_2H_3O_2^- + Fe^{+++} \rightarrow HC_2H_3O_2 + FePO_4$$

Moreover, if the reaction takes place in a boiling, dilute solution, the excess of the iron can be precipitated as basic ferric acetate. If the solution is filtered hot, a filtrate is obtained which is free from iron and from phosphoric acid. If, however, it cools, some of the iron goes back into solution and, since ferric phosphate is appreciably soluble in ferric acetate solution, some of the phosphoric acid also goes into solution.

Since ferric phosphate, unlike the phosphates of the alkaline earths, is insoluble in acetic acid, it is evident that phosphoric acid may be removed from a solution of alkaline earth phosphate in acetic acid by adding ferric chloride and an excess of soluble acetate and boiling.

To accomplish this, dissolve the phosphate in as little hydrochloric acid as possible, add ammonium carbonate until a slight permanent precipitate is obtained, and dissolve the precipitate by adding 1 or 2 drops of 6-normal hydrochloric acid. Add an excess of ammonium acetate and ferric chloride, drop by drop, until the solution above the yellowish white precipitate of ferric phosphate is colored distinctly brown by colloidal ferric hydroxide. Dilute with considerable water, heat to boiling, and filter while hot. To detect phosphoric acid in the precipitate dissolve it in nitric acid, evaporate the solution to a small volume, and treat with ammonium molybdate solution; a yellow, crystalline precipitate of ammonium phosphomolybdate proves the presence of phosphoric acid. Or dissolve the iron precipitate in hydrochloric acid, add 2 g of tartaric acid to prevent the precipitation of iron, add ammonia in

excess, and then add some magnesium ammonium chloride mixture. A white precipitate of magnesium ammonium phosphate shows the presence of phosphoric acid.

8. **Lead Acetate** precipitates white lead phosphate, nearly insoluble in acetic acid:

$$2\ HPO_4^{--} + 3\ Pb^{++} + 2\ C_2H_3O_2^{-} \rightarrow 2\ HC_2H_3O_2 + \mathbf{Pb_3(PO_4)_2}$$

9. **Magnesia Mixture** (an aqueous solution of ammonium chloride, ammonia, and magnesium chloride) precipitates from very dilute solutions white, crystalline magnesium ammonium phosphate, $MgNH_4PO_4 + 6\ H_2O$,

$$HPO_4^{--} + Mg^{++} + NH_3 \rightarrow \mathbf{MgNH_4PO_4}$$

which is soluble in all acids, but practically insoluble in dilute 2½ per cent ammonia (cf. p. 273).

10. **Metastannic Acid.** — If metallic tin is added to a nitric acid solution of phosphoric acid, or a phosphate, the tin is changed to metastannic acid, which unites with the phosphoric acid, forming an adsorption compound. This reaction is often used to remove phosphoric acid from an acid solution without the introduction of cations.

The precipitate has been regarded as metastannic acid and stannic phosphate or as a complex phosphostannic acid, but Werner Mecklenberg* has shown that the phenomenon is one of adsorption rather than true chemical combination. The precipitation of the phosphoric acid can be accomplished by the addition of colloidal stannic hydroxide, previously formed by the treatment of tin with nitric acid. The presence of hydrochloric acid *peptizes* or dissolves the adsorption compound so that the reaction will not take place if much hydrochloric acid is present. According to Gottermann and Schindhelm† phosphoric acid can be precipitated from *dilute* hydrochloric solutions by a cold, concentrated, freshly prepared solution of stannic chloride (2 or 3 g $SnCl_4$ to 0.5 g H_3PO_4).

11. **Mercurous Nitrate** precipitates from neutral solutions white mercurous phosphate, soluble in nitric acid but insoluble in acetic acid.

12. **Zinc,** in acid solutions, does not reduce phosphoric acid (difference from phosphorous and hypophosphorous acids).

13. **Zirconium Oxychloride,** $ZrOCl_2$, precipitates white $Zr(HPO_4)_2$ from slightly acid solutions. The excess reagent can be removed by adding ammonia which precipitates $Zr(OH)_4$, and after short boiling the $Zr(OH)_4$ and $Zr(HPO_4)_2$ are insoluble in dilute acids.

DETECTION OF PHOSPHORUS IN IRON AND STEEL

Phosphorus is present in iron and steel as iron phosphide, but only to a slight extent (usually less than 0.1 per cent). To detect the phosphorus it is necessary to oxidize it to phosphoric acid and then use one of the above reactions. Since, however,

* *Z. anal. Chem.*, **52**, 293 (1913).

† *Ber.*, **49**, 2416; *Z. anal. Chem.*, **56**, 205 (1917).

very small amounts of phosphorus are present, it is necessary to start with a large amount of the original substance in order to obtain a perceptible phosphorus test. It is best to proceed as follows: Dissolve 5 to 10 g of the iron or steel in 60 ml of 6-normal nitric acid,* evaporate the solution to dryness and ignite over a free flame (with constant stirring) until no more red fumes are given off. All organic matter is thereby destroyed, silicic acid is dehydrated, and the oxidation of the phosphorus to phosphoric acid is completed. After cooling, dissolve the oxides in 50 ml of 12-normal hydrochloric acid (warming gently), evaporate off the excess of acid, dilute, and filter off the silica. In the filtrate all the iron and all the phosphoric acid will be found, and the phosphoric acid may be detected by either the molybdate or the magnesia-mixture reaction. To detect it according to the former method, evaporate to dryness the filtrate obtained after the removal of the silica, dissolve the residue in as little 6-normal nitric acid as possible, add 50 ml of ammonium molybdate solution and 15–20 ml of a 75 per cent ammonium nitrate solution, heat the mixture gently, shake or stir vigorously, and allow it to stand an hour. A yellow, crystalline precipitate shows the presence of phosphorus.

To detect the phosphorus according to the magnesia-mixture method, it is necessary first to remove the greater part of the iron. Neutralize the hydrochloric acid filtrate with ammonia, add a saturated solution of sulfur dioxide, and boil the solution, whereby the previously dark-colored solution is either decolorized or becomes a light green. Add 20 ml of 12-normal hydrochloric acid, and boil the solution until the excess of sulfur dioxide is expelled. By this operation all the ferric salt is reduced to ferrous salt. Add a few drops of chlorine water (which forms a little ferric salt), neutralize with ammonia, and dilute to about a liter; add 3 ml of a saturated solution of ammonium acetate and 5 ml of acetic acid, and heat the solution to boiling. All the ferric salt and all the phosphoric acid will be precipitated in the form of ferric phosphate and basic ferric acetate, while the greater part of the iron remains in solution as ferrous salt. Filter off the light brown precipitate through a small plaited filter, wash it with hot water, and dissolve in dilute hydrochloric acid. Evaporate the solution almost to dryness, add 2 g of citric (or tartaric) acid (which should be dissolved in as little water as possible), add an excess of ammonia, and precipitate the phosphoric acid by the addition of magnesia mixture. A white, crystalline precipitate shows the presence of phosphoric acid.

Reactions in the Dry Way

The tertiary salts of the alkalies melt without decomposition; the secondary salts lose water and are changed to pyrophosphates while the primary salts form a glassy metaphosphate.

The so-called "salt of phosphorus," or "microcosmic salt," $NaNH_4HPO_4 \cdot 4\ H_2O$, which is much used as a reagent, loses water and ammonia on being fused, forming a clear glass of sodium metaphosphate:

$$NaNH_4HPO_4 \cdot 4\ H_2O \rightarrow 5\ H_2O \uparrow + NH_3 \uparrow + NaPO_3$$

If the salt is heated in the loop of a platinum wire, a clear bead is obtained — the so-called "salt of phosphorus" bead.

* If the sample were dissolved in HCl or H_2SO_4, part or all of the phosphorus would escape as phosphine instead of being oxidized to H_3PO_4.

Just as metaphosphoric acid unites with water, on boiling its solution, forming orthophosphoric acid,

$$HPO_3 + H_2O \rightarrow H_3PO_4$$

so sodium metaphosphate dissolves, at the fusion temperature, a great many metallic oxides, forming characteristically colored orthophosphates,

$$NaPO_3 + CuO \rightarrow NaCuPO_4 \text{ (blue bead)}$$

which may be changed in the reducing flame to metaphosphate again:

$$NaCuPO_4 + C \rightarrow CO + \underbrace{Cu + NaPO_3}_{\text{Brownish red opaque bead}}$$

Many anhydrous phosphates are reduced by heating with magnesium to phosphides, which, on being breathed upon, give the peculiar odor of phosphine:

$$Ca_3(PO_4)_2 + 8\ Mg \rightarrow 8\ MgO + Ca_3P_2$$
$$Ca_3P_2 + 6\ H_2O \rightarrow 3\ Ca(OH)_2 + 2\ PH_3\uparrow$$

Hypophosphoric Acid, $H_4P_2O_6 \cdot 2\ H_2O$

Preparation and Properties. — This acid, which is of some importance in analytical chemistry, can be formed by the slow oxidation of white phosphorus in moist air, by heating white phosphorus with copper nitrate solution, or by anodic oxidation of copper phosphide in dilute sulfuric acid. By careful neutralization with sodium carbonate and sodium acetate, the difficultly soluble acid salt, $Na_2H_2P_2O_6 \cdot 4\ H_2O$, crystallizes out. It is also possible to prepare crystals of $Na_5HP_2O_6 \cdot 9\ H_2O$ and of $Na_4P_2O_6 \cdot 10\ H_2O$.

The free acid crystallizes in orthorhombic needles corresponding to the composition $H_4P_2O_6 \cdot 2\ H_2O$. Its solutions are strongly acidic although the conductivity indicates only slight ionization. When all four hydrogen atoms are replaced by sodium, the compound formed hydrolyzes in aqueous solution to give a distinctly basic reaction.

From molecular-weight determinations, it appears that the formula $H_4P_2O_6$ is better than H_2PO_3 although in some cases the simple molecule undoubtedly exists. The structure is usually assumed to be $(HO)_2OP \cdot PO(OH)_2$.

The acid has a strong tendency to form mixed salts with alkali and zinc, copper, manganese, etc.

Thorium Hypophosphate, ThP_2O_6, is insoluble in strong hydrochloric acid, and for this reason hypophosphoric acid has been used to separate thorium from other rare earths. Quadrivalent titanium, zirconium, and cerium give similar precipitates in acid solutions, but the thorium precipitate, unlike zirconium hypophosphate, is not soluble in oxalic acid and is precipitated in the presence of hydrogen peroxide which prevents the precipitation of titanium by oxidizing it to pertitanic acid and of cerium by reducing it to cerous salt.

The polarity of phosphorus is +4 in hypophosphoric acid but it is not easily oxidized. It does not reduce gold or silver solution and it is not acted upon by hydrogen peroxide or chromic acid in aqueous solutions. If permanganate is added to hypophosphoric acid in the presence of considerable sulfuric acid, the purple color of the permanganate remains unchanged for some time. If, however, the solution is heated it is suddenly decolorized and the following reaction takes place:

$$2\ MnO_4^- + 5\ H_4P_2O_6 + 6\ H^+ + 2\ H_2O \rightarrow 2\ Mn^{++} + 10\ H_3PO_4$$

Hypophosphoric acid is not reduced by zinc and dilute sulfuric acid (difference from H_3PO_2 and H_3PO_3) and gives with silver nitrate a white precipitate which does not darken in the light (difference from H_3PO_2 and H_3PO_3).

PHOSPHORUS, P. At. Wt. 31.02, At. No. 15

Mol. Wt. P_4 124.08. M. P. 44.1°

Occurrence. — Phosphorus is found in nature only in the form of phosphates, of which calcium phosphate is the most important. It occurs as apatite, $Ca_5(PO_4)_3(Cl,F)$, in hexagonal crystals, and in an impure state as phosphorite, which is used extensively as a fertilizer. Calcium phosphate is also an important constituent of bones and the seeds of plants.

A very interesting occurrence of phosphorus is pyromorphite (cf. p. 110), isomorphous with apatite, vanadinite, and mimetesite.

Properties. — Phosphorus exists in four allotropic forms: (*a*) Ordinary or colorless phosphorus. (*b*) Red, crystalline phosphorus. (*c*) Bright red phosphorus. (*d*) Black, crystalline phosphorus.

Ordinary phosphorus is poisonous, is colorless when pure (it becomes yellow on exposure to the light, and is coated with a layer of red phosphorus), melts at 44° C, and ignites at 60° C in the air, so that it must be kept covered with water, in which it is insoluble. It is readily soluble in carbon disulfide, and slightly soluble in ether. It is easily oxidized by nitric acid to phosphoric acid:

$$3\ P_4 + 20\ HNO_3 + 8\ H_2O \rightarrow 12\ H_3PO_4 + 20\ NO\uparrow$$

The colorless phosphorus, but not the red modification, is oxidized to hypophosphorous and phosphorous acids by exposure to moist air. This causes the characteristic phosphorous odor, and, in the dark, a pale green luminescence. If phosphorus vapors, or phosphine, are allowed to act upon moist silver nitrate paper, they blacken it, on account of the formation of silver phosphide and metallic silver. The reaction probably takes place in this way: First, the phosphorus reacts with water to form phosphine and hypophosphorous acid,

$$P_4 + 6\ H_2O \rightarrow 3\ H_3PO_2 + PH_3\uparrow\ *$$

which then react with the silver nitrate:

$$H_3PO_2 + 2\ H_2O + 4\ AgNO_3 \rightarrow 4\ HNO_3 + H_3PO_4 + 4\ Ag$$

$$PH_3 + 3\ AgNO_3 \rightarrow 3\ HNO_3 + Ag_3P$$

This exceedingly sensitive reaction for *colorless* phosphorus was discovered by Scheuer.† It is a decisive test only when no other substance is present, such as H_2S, H_3As, H_3Sb, formaldehyde, or formic acid, which is capable of reacting with silver nitrate.

Red phosphorus is crystalline (hexagonal, rhombohedral), and is formed by heating ordinary phosphorus to about 250° out of contact with the air. It is not poisonous, is insoluble in carbon disulfide, and does not ignite until heated to 256°. It is non-luminous in the dark, does not oxidize in the air, but is readily oxidized by nitric acid to phosphoric acid.

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* Phosphorus and water by themselves do not react in accordance with this equation, but it seems probable that they do in the presence of silver nitrate.

† *Ann. Chem. Phys.*, **112**, 214 (1859).

Light-red phosphorus is obtained, according to Schenk,* by heating a solution of white phosphorus in phosphorus tribromide for hours with a return-flow condenser. The phosphorus which then separates is of a light red color, is not poisonous, but enters into reaction so readily that it is easily distinguished from red phosphorus. It dissolves in concentrated potassium or sodium hydroxide with a stormy evolution of phosphine, the reaction taking place even more readily than with white phosphorus. When covered with ammonia, it blackens.

Black phosphorus is obtained when red phosphorus and lead are heated together in a sealed tube to a red heat and the mass treated with dilute nitric acid after it is cold; the lead dissolves and leaves the phosphorus as black phosphorus. By heating to 360° it is changed to ordinary phosphorus again.

Phosphorus is found in a great many organic substances. In order to detect its presence, the compound is heated in a sealed tube with fuming nitric acid, which destroys the organic matter and oxidizes the phosphorus to phosphoric acid (detected by any of the above reactions).

Arsenious, arsenic, and chromic acids, which also belong to this group of acids, have already been described on pp. 143, 147, and 199.

SPECIAL PROCEDURES FOR PHOSPHORUS

Mitscherlich Test for White, Poisonous Phosphorus†

This sensitive test is based upon the luminescence of white phosphorus when exposed to moist air in the dark. It is used to detect phosphorus in cases of poisoning.

Procedure. — Place the food residues, or finely cut pieces of the body, in the liter flask *K* (Fig. 17) and add enough water to form a thin paste. Then, while shaking the flask, add tartaric acid to slightly acid reaction, in order to combine with any ammonia present. Connect the tube *R* with the flask and heat the contents to boiling. Carry out this operation in a dark room. As the vapors condense in the tube *A*, a greenish luminous zone is visible even when only a few milligrams of phosphorus are present. If larger quantities of phosphorus are at hand, the distillate in the flask *B* contains tiny globules of phosphorus which, by gently heating and rotating the liquid, can be made to collect into a larger drop; the aqueous solution also contains phosphorous acid which can be detected by the method of Blondlot-Dusart (see p. 408).

If, therefore, the luminosity is apparent during the distillation in the dark, then the presence of white phosphorus is probable but not certain, because phosphorus subsulfide, P_4S_3, sometimes used as a substitute for phosphorus in the manufacture of matches, will often cause luminescence in the Mitscherlich apparatus‡ especially if a little zinc oxide is added to the liquid in *K* to combine with H_2S, which tends to prevent the luminescence.

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* *Ber.*, **36**, 979 (1903).

† *J. pr. Chem.*, **66**, 238 (1855).

‡ I. Mai and F. Schaffer, *Ber.*, **1903**, 870; L. Vignon, *Bull. soc. chem.* [3], **33**, 805 (1905), and Schenk and Scharff, *Ber.*, **1906**, 1522. Not all commercial preparations of P_4S_3 show luminescence in the Mitscherlich apparatus. Thus a sample from Kahlbaum did not show the slightest luminescence by boiling with water or with concentrated salt solution. It was very pure and contained 55.82 per cent P and 44.14 per cent S.

If the luminescence is not apparent, it is not certain that white phosphorus is absent; traces of ammonia, hydrogen sulfide, alcohol, ethereal oils, and unsaturated hydrocarbons interfere with the test. In such cases it is advisable not to stop distilling too soon, as it often happens that the interfering substances will distil over and then the luminescence will appear. If no luminescence is noticed, examine the dis-

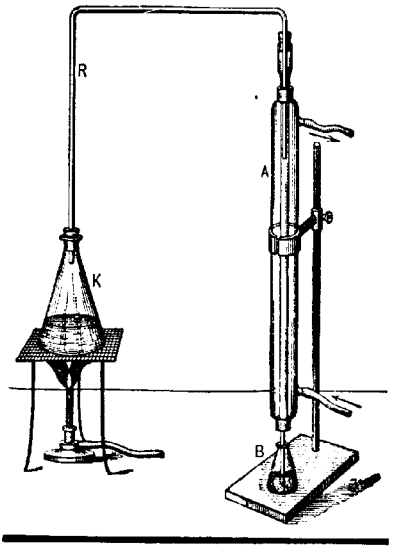


FIG. 17

tillate. Treat a part of it with strong chlorine water, evaporate to small volume on the water-bath, and then test for phosphoric acid. Cf. pages 400 and 402.

According to J. Peset* the luminosity is very distinct in the flask if the liquid is heated to boiling, allowed to cool somewhat, and again boiled. In this way 0.004 mg of phosphorus can be detected.

DETECTION OF PHOSPHORUS AND PHOSPHOROUS ACID ACCORDING TO BLONDLOT-DUSART†

This beautiful method is based upon Dusart's observation that hydrogen containing phosphine, when allowed to flow from a tube provided with a platinum tip, will burn with a flame having an emerald-green core. The green color is particularly apparent upon holding a cold porcelain dish in the flame.

Since phosphorus, phosphorous acid, and hypophosphorous acid (not phosphoric acid) are easily reduced to phosphine by zinc and dilute sulfuric acid, it is merely

* *Z. anal. Chem.*, **48**, 35 (1909).

† L. Dusart, *Compt. rend.*, **43**, 1126 (1856), and Blondlot, *J. pharm. chim.* [3], **40**, 25 (1854).

necessary to pass the evolved gas through a tube with a platinum tip, and light it when all the air is expelled; the merest trace of phosphorus is recognized by the green color.

Inasmuch as organic matter can prevent the appearance of the green flame, the phosphorus is first separated from it as follows: Place the solution containing the phosphorus, or the distillate obtained by the Mitscherlich test, in a gas-evolution flask, add zinc (free from phosphorus) and dilute sulfuric acid (1 : 7), and pass the evolved gas into a neutral solution of silver nitrate; if phosphorus is present a

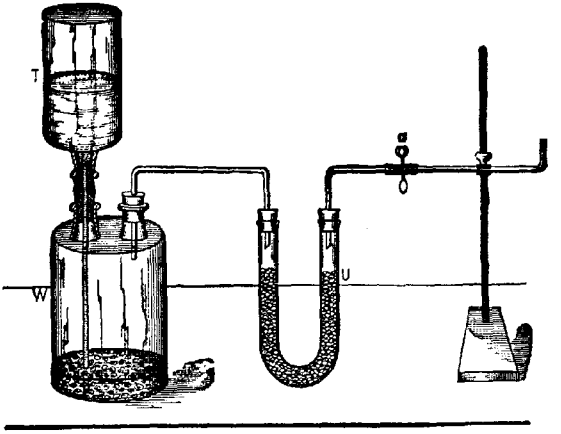


FIG. 18

black precipitate of silver phosphide is obtained, which, if hydrogen sulfide was present, may contain silver sulfide. Filter off this precipitate, wash it well with water, and place it in the Blondlot apparatus (Fig. 18). In the 500-ml Woulfe bottle, *W*, generate hydrogen by means of zinc, free from phosphorus, and dilute sulfuric acid (1 : 7). The tube *U* contains pieces of pumice wet with concentrated potassium hydroxide solution. After the air is entirely expelled from the apparatus, close the pinchcock *a*, which causes the acid to rise into the reservoir *T* (a bottle with the bottom cut off). Now open the cock *a* wide enough to permit a steady stream of hydrogen to pass out from the delivery tube, which is made of potash-glass and is provided with a platinum tip.* The flame from the lighted gas should not be too large.

If the flame shows no green luminescence in the dark when a porcelain dish is held in it, then the hydrogen gas is free from phosphorus and can be used for the test. Rinse the black silver precipitate through *T* into the bottle *W*. If the precipitate contained phosphorus, the core of the flame becomes green, particularly noticeable upon holding a porcelain dish in it. Any hydrogen sulfide evolved collects in the U-tube, *U*.

* A small blowpipe tip can be used here or, still better, a cylinder made by rolling together some platinum foil.

Since both the Mitscherlich and the Blondlot-Dusart tests give indications not only of white phosphorus, but also of phosphorus subsulfide, it was desirable to have a test to serve for the identification of white phosphorus with certainty even when the sulfide is also present. For this purpose, R. Schenk and E. Scharff* make use of the property that white phosphorus has of ionizing the atmosphere, a property which the sulfide does not possess. They use the Elster-Geitel apparatus for this purpose. For details of the test the original paper must be consulted.

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* R. Schenk and E. Scharff, *Ber.*, **1906**, 1522. For the detection of white phosphorus in the presence of hypophosphorous and arsenious acids see A. Leclive, *Chem. Zentr.*, **1912**, I, 684.

THIOSULFURIC ACID, $H_2S_2O_3$

This very unstable acid, in which one atom of sulfur has a positive valence of six and the other a negative valence of two, is soon decomposed, even in dilute aqueous solution, into sulfurous acid and sulfur:

$$H_2S_2O_3 \rightarrow H_2SO_3 + S$$

Free thiosulfuric acid is unknown in the pure state although in absolute alcohol the following reaction can take place:

$$H_2S \text{ (dry)} + PbS_2O_3 \text{ (dry)} = PbS + H_2S_2O_3$$

When an aqueous solution of a thiosulfate is treated with acid, it soon becomes turbid from precipitation of sulfur which, in this case, often appears yellowish. The salts of thiosulfuric acid, the thiosulfates, are much more stable than the free acid.

Thiosulfuric acid has been erroneously called *hyposulfurous acid*, and this wrong nomenclature still causes much confusion in chemical literature (cf. p. 356).

Hyposulfurous acid. — Hyposulfurous acid is really $H_2S_2O_4$ and was first prepared by Berthollet in 1789 when he showed that when iron was left in contact with an aqueous solution of sulfur dioxide it dissolved without any evolution of hydrogen, and Schönbein later showed that the acid had strong reducing properties; the sodium salt today finds commercial use for that reason. This was first obtained by Schutzenberger, in 1869, by the action of zinc on a concentrated solution of sodium bisulfite and separating it from the sulfites by fractional precipitation:

$$Zn + 4\ NaHSO_3 \rightarrow Na_2S_2O_4 + ZnSO_3 + Na_2SO_3 + 2\ H_2O$$

A solution of the free acid can be obtained by adding oxalic acid to sodium hyposulfite solution. This solution has a yellow color and decomposes into free sulfur and sulfur dioxide:

$$H_2S_2O_4 \rightarrow H_2O + S + SO_2$$

Formation of Thiosulfates

1. By boiling sulfur with an alkali or alkaline earth hydroxide:

$$4\ S + 6\ OH^- \rightarrow 2\ S^{--} + S_2O_3^{--} + 3\ H_2O$$

This reaction is analogous to the action of the halogens and of phosphorus upon hydroxides, forming chloride and hypochloride, phosphide (phosphine) and hypophosphite, etc. (cf. pp. 305 and 362).

2. By boiling sulfites with sulfur:

$$SO_3^{--} + S \rightarrow S_2O_3^{--}$$

3. By treating alkali polysulfides with alkali sulfite in the cold:

$$Na_2S_5 + 4\ Na_2SO_3 \rightarrow 4\ Na_2S_2O_3 + Na_2S$$

4. By the oxidation of polysulfides:

$$2\ Na_2S_2 + 3\ O_2 \rightarrow 2\ Na_2S_2O_3$$

This last reaction takes place on boiling the solution of polysulfide in the air, or very slowly on standing. Yellow ammonium polysulfide is changed, on standing in the air, into ammonium thiosulfate with deposition of sulfur.

Aqueous solutions of alkali thiosulfate usually become turbid on standing. This has been attributed to the action of CO_2 but in most cases it is caused by bacteria. Sterile solutions of thiosulfates are quite stable.

The most important commercial thiosulfate is the sodium salt $Na_2S_2O_3 \cdot 5\,H_2O$, the well-known "hypo" of photographers.

Solubility. — The thiosulfates of the alkalies are readily soluble in water, the remaining ones are difficultly soluble; many of them dissolve in an excess of sodium thiosulfate, forming complex ions. The thiosulfates of the metals of the silver and copper groups are decomposed, as a rule, into insoluble sulfide by contact with boiling water so that sodium thiosulfate can replace hydrogen sulfide as a precipitant in many cases. In this respect, however, it is not so efficient as ammonium thioacetate.

Reactions in the Wet Way

Use a solution of sodium thiosulfate for these reactions.

1. **Sulfuric Acid.** — Both dilute and concentrated sulfuric acid decompose thiosulfates, with deposition of sulfur.

2. **Silver Nitrate** produces a white precipitate, which rapidly becomes yellow, brown, and finally black, owing to the formation of silver sulfide:

$$S_2O_3^{--} + 2\,Ag^+ \rightarrow \mathbf{Ag_2S_2O_3}$$

$$\mathbf{Ag_2S_2O_3} + H_2O \rightarrow H_2SO_4 + \mathbf{Ag_2S}$$

Silver thiosulfate is soluble in an excess of the reagent. Difficultly soluble $Na[AgS_2O_3]$ is at first formed,

$$\mathbf{Ag_2S_2O_3} + S_2O_3^{--} \rightarrow 2\,[AgS_2O_3]^-$$

which combines with more thiosulfate, forming a soluble complex salt:

$$2[AgS_2O_3]^- + S_2O_3^{--} \rightarrow [Ag_2(S_2O_3)_3]^{---}$$

But by boiling the dilute solution, silver sulfide is precipitated:

$$[Ag_2(S_2O_3)_3]^{---} \rightarrow S_2O_3^{--} + SO_4^{--} + SO_2\uparrow + S + \mathbf{Ag_2S}$$

Many other metals behave like silver, especially those of the hydrogen sulfide group. Thus copper, mercurous, and tin salts are precipitated as sulfides by boiling the acid solutions with sodium thiosulfate.*

3. **Ammonium Molybdate,** in 10 per cent solution, mixed with an equal volume of thiosulfate solution and poured upon some concentrated sulfuric acid in a test tube, gives a blue ring at the contact zone.

4. **Barium Chloride** in excess produces a white, crystalline precipitate of barium thiosulfate,† difficultly soluble in cold water (500 ml of water at 18° dissolves about 1 g of BaS_2O_3), but fairly soluble in hot water.

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* *Z. anorg. Chem.*, **28**, 223 (1902).

† Rubbing the inside walls of the test tube hastens the formation of this precipitate.

5. **Cupric Salts** are reduced to colorless cuprous compounds, with the formation of sodium tetrathionate:

$$2\ S_2O_3^{--} + 2\ Cu^{++} \rightarrow Cu_2^{++} + S_4O_6^{--}$$

The unstable cuprous sulfate immediately acts upon more thiosulfate, forming sodium cuprous thiosulfate:

$$Cu_2^{++} + 2\ S_2O_3^{--} \rightarrow [Cu_2(S_2O_3)_2]^{--}$$

If the colorless solution of the cuprous salt is treated with caustic potash solution, yellow cuprous hydroxide is in some cases formed immediately, in other cases only on standing or on warming. The precipitate becomes darker colored on being boiled. If the solution is acidified and boiled, black cuprous sulfide is precipitated.

The colorless solution of the cuprous salt also gives with potassium ferrocyanide a white (usually a light pink) precipitate of cuprous ferrocyanide.

6. **Ferric Chloride** produces, in solutions of sodium thiosulfate, at first a dark violet coloration (perhaps ferric thiosulfate), which disappears after some time, leaving a colorless solution containing ferrous chloride and sodium tetrathionate:

$$2\ S_2O_3^{--} + 2\ Fe^{+++} \rightarrow 2\ Fe^{++} + S_4O_6^{--}$$

7. **Iodine Solution** is decolorized by a thiosulfate solution:

$$2\ S_2O_3^{--} + I_2 \rightarrow 2\ I^- + S_4O_6^{--}$$

The iodine is reduced to iodine anions and the thiosulfate ion is oxidized to tetrathionate ion.

Chlorine and bromine in excess (cf. p. 319) act quite differently upon thiosulfates. If chlorine (or bromine) is conducted into a solution of sodium thiosulfate, a considerable precipitation of sulfur takes place, which, upon further action of the halogen, disappears:

$$S_2O_3^{--} + H_2O + Cl_2 \rightarrow 2\ Cl^- + 2\ H^+ + SO_4^{--} + S$$
$$S + 4\ H_2O + 3\ Cl_2 \rightarrow 8\ H^+ + 6\ Cl^- + SO_4^{--}$$

8. **Lead Acetate** precipitates white lead thiosulfate, soluble in an excess of the alkali thiosulfate. On boiling the solution a voluminous precipitate, consisting of lead sulfate and lead sulfide, is formed.

9. **Permanganate** is at once decolorized by an acid solution of thiosulfate. The complete oxidation of the thiosulfate corresponds to the formation of sulfate:

$$8\ MnO_4^- + 5\ S_2O_3^{--} + 14\ H^+ \rightarrow 8\ Mn^{++} + 10\ SO_4^{--} + 7\ H_2O$$

10. **Potassium Chromate** in acid solution is at once reduced to chromic salt:

$$8\ CrO_4^{--} + 3\ S_2O_3^{--} + 34\ H^+ \rightarrow 8\ Cr^{+++} + 6\ SO_4^{--} + 17\ H_2O$$

In neutral solution a brown precipitate of chromic hydroxide and sulfur is obtained:

$$2\,CrO_4^{--} + 3\,S_2O_3^{--} + 5\,H_2O \rightarrow 3\,SO_4^{--} + 4\,OH^- + 3\,S + 2\,Cr(OH)_3$$

11. **Potassium Cyanide.** — Boiling a solution of a thiosulfate with potassium cyanide and caustic soda transforms the thiosulfate into sulfite and the cyanide into thiocyanate:

$$S_2O_3^{--} + CN^- \rightarrow SO_3^{--} + CNS^-$$

On acidifying the solution with hydrochloric acid and adding ferric chloride, the blood-red color of ferric thiocyanate is obtained (difference from sulfites).

12. **Sodium Nitroprusside** which has been exposed in aqueous solution to air and sunlight until the solution is brown, or which has been treated with one or two drops of potassium ferricyanide solution and a like quantity of sodium hydroxide, gives a deep blue coloration which, on standing, heating, or the addition of a little potassium ferricyanide, is intensified (difference from sulfites and tetrathionates).

13. **Strontium Chloride** produces a white, crystalline precipitate, but only in very concentrated solutions (3.7 ml of water at 18° dissolves 1 g of SrS_2O_3).

14. **Zinc,** in acid solution, causes the evolution of hydrogen sulfide and formation of some hydrosulfurous acid, $H_2S_2O_4$, in solution:

$$3\,Zn + 2\,H_2S_2O_3 + 6\,H^+ \rightarrow 3\,Zn^{++} + H_2S_2O_4 + 2\,H_2O + 2\,H_2S\uparrow$$

15. **Zinc Salts** produce no precipitate (difference from sulfides).

16. **Zinc Sulfate** and **Sodium Nitroprusside** produce no red coloration (difference from sulfites).

DETECTION OF SULFUROUS AND THIOSULFURIC ACIDS IN THE PRESENCE OF HYDROGEN SULFIDE

Method of E. Votoček.* *Principle.* — Alkali sulfites, sulfides, and polysulfides in slightly alkaline solution will decolorize fuchsin, malachite green, or a mixture of these two dyestuffs. If a solution of acetaldehyde or of formalin is added to the decolorized solution, the color returns. Sulfhydrates, thiosulfates, and thionates do not decolorize a solution of the above dyestuffs.

Reagent. — Dissolve 0.025 g of fuchsin and 0.025 g of malachite green separately in 100 ml portions of water. Mix three volumes of the fuchsin solution with one volume of the malachite green solution.

Procedure. — It is assumed that the solution is slightly alkaline. Test the solution first for sulfide (monosulfide, sulfhydrate, and polysulfide) by treating a little of it with 2 or 3 drops of sodium nitroprusside solution. A reddish violet color shows

* *Ber.*, **40**, 414 (1907).

the presence of the sulfide anion. If sulfide is present, treat the remainder of the solution with cadmium carbonate, shake vigorously, and allow the cadmium sulfide to settle somewhat. Filter and test a new portion of the filtrate with sodium nitroprusside to see if all the sulfide has been removed. When the sulfide has been removed or proved absent, treat the remainder of the filtrate with a drop of phenolphthalein solution and introduce carbon dioxide gas until the solution is decolorized by it. Take 2 or 3 ml of this colorless solution and test it with 2 or 3 drops of the fuchsin-malachite-green reagent. If the solution of the dyestuffs is decolorized, a sulfite is present. To the remainder of the solution add a little dilute hydrochloric acid, boil a few minutes, and notice whether there is any deposition of sulfur. If the solution remains clear, no thiosulfate is present.

This is the best method for detecting a sulfide, a sulfite, and a thiosulfate in the presence of one another.

Method of Autenrieth and Windaus.* — The three acids are assumed to be present together in solution in the form of their alkali salts. Treat the fairly concentrated solution with cadmium carbonate, shake, and filter off the excess cadmium carbonate and any cadmium sulfide which will be formed if a sulfide is present. Treat the filtrate with strontium nitrate solution and allow it to stand over night. Filter off any strontium sulfite that may be formed and wash it with a little cold water. If the strontium sulfite is treated on the filter with dilute hydrochloric acid, sulfurous acid goes into solution, which can be detected by its property of decolorizing an iodine solution. The thiosulfate remains in the filtrate from the strontium sulfite; it can be detected by acidifying with hydrochloric acid and warming, when sulfur will be deposited.

Solubility of Sulfites and Thiosulfates of the Alkaline Earths in Water

	Sulfite	Thiosulfate
Calcium	1 : 800	1 : 2
Strontium	1 : 30,000	1 : 3.7
Barium	1 : 46,000	1 : 480

Reactions in the Dry Way

The thiosulfates of the alkalies, on being heated out of contact with the air, are changed into sulfate and polysulfide, and the latter into sulfide and sulfur:

$$4\ Na_2S_2O_3 \rightarrow 3\ Na_2SO_4 + Na_2S_5$$

$$Na_2S_5 \rightarrow Na_2S + 4\ S$$

If this reaction is performed in a closed tube, a sublimate of sulfur is obtained (difference from sulfites); and the residue yields hydrogen sulfide if treated with acid.

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* *Z. anal. Chem.*, **1898**, 295. For another method of detecting sulfite in the presence of thiosulfate, cf. F. E. Weston, *Chem. Zentr.*, **1910**, I, 379.

GROUP V

Silver Nitrate produces no precipitate in acid or neutral solutions.
Barium Chloride, also, causes no precipitation.

NITRIC ACID, HNO_3

Occurrence. — Nitric acid is found in the form of nitrates in small amounts almost everywhere in nature; thus the ammonium salt is found in the atmosphere and in soils; the calcium salt is found in old masonry; the sodium salt is found in rainless localities, particularly in Chile (Chile saltpeter).

Nitric acid is the final product of the oxidation of ammonia; it is found wherever nitrogenous organic substances have been subjected to decay, forming ammonia. With the help of microörganisms (*Monas nitrificans*, according to Winogradsky) the ammonia is changed first to nitrous acid,

$$2\ NH_3 + 3\ O_2 \rightarrow 2\ H_2O + 2\ HNO_2$$

and by further oxidation to nitric acid:

$$2\ HNO_2 + O_2 \rightarrow 2\ HNO_3$$

Properties. — Pure nitric acid is a colorless liquid, with a density of 1.54 at 20°. It has been condensed to white crystals below −41°, and on melting there is slight decomposition into H_2O and N_2O_5. At 86° it begins to boil, with decomposition, giving off its anhydride, which suffers further decomposition into nitrogen dioxide, NO_2 (brown fumes), and oxygen. By the constant loss of N_2O_5, the nitric acid becomes more and more dilute and the boiling point constantly rises, until at 120.5° C it remains constant; nitric acid of density 1.414 distils over, forming a 68 per cent acid. If a more dilute acid is subjected to distillation, water is at first given off, the boiling point constantly rising until 120.5° C is reached, when a 68 per cent acid again distils unchanged.

Red, *fuming nitric acid* is obtained by conducting NO_2 into the colorless, concentrated acid. In its most concentrated condition it possesses a density of 1.55.

If the fuming acid is treated with water, it is colored green, and vapors of nitric oxide are given off, which are colored brown on coming in contact with the air. The dissolved NO_2 (or, better, N_2O_4), being a mixed anhydride, is changed into nitric and nitrous acids,

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$$

and the nitrous acid, owing to the heat of reaction, is partly changed into nitric acid, with evolution of nitric oxide,

$$3\ HNO_2 \rightarrow H_2O + HNO_3 + 2\ NO\uparrow$$

and

$$2\ NO + O_2 \rightarrow 2\ NO_2\uparrow \text{ (brown vapors)}$$

Nitric acid is a strong oxidizing agent (cf. p. 61). It is monobasic, and, like the halogen acids, is one of the strongest acids (cf. p. 11). It forms stable salts, all of

which are soluble in water; but a few of them are changed by water into basic salts (cf. bismuth and mercuric salts), insoluble in water, but soluble in dilute nitric acid.

Nitric acid oxidizes and dissolves all metals except chromium, aluminum, gold, and the platinum metals. It forms nitrates except with tin, antimony, and arsenic. With copper, silver, lead, and mercury the usual reaction is to form the nitrate of the metal and nitric oxide, NO. With zinc the products vary with the conditions; as reduction products NO_2, NO, N_2, $NH_2OH \cdot HNO_3$, and NH_4NO_3 are formed depending upon the concentration and quantity of acid used. Ferrous hydroxide can cause complete reduction of the nitrate ion to ammonia, but in the presence of sulfuric acid, ferrous sulfate causes reduction only to nitric oxide. Carbon (not graphite) is oxidized to CO_2 by hot, concentrated acid. Oxalic acid is oxidized to water and CO_2. $H_4Fe(CN)_6$ is oxidized to $H_3Fe(CN)_6$ and then to nitroso-ferricyanic acid, $H_2Fe(CN)_5NO$, of which the sodium salt, $Na_2Fe(CN)_5NO \cdot H_2O$, is commonly called *sodium nitroprusside* and is used as reagent in detecting sulfur. HCNS is oxidized by nitric acid, and the sulfur is converted to sulfate. Phosphorus and its compounds in which the phosphorus has a valence lower than five are oxidized to H_3PO_4. Hydrochloric acid and nitric acid form aqua regia which decomposes into NO and Cl_2 or into NOCl and Cl_2. Hydrobromic acid is oxidized to free bromine, but with hydriodic acid the iodine which is first formed is oxidized to HIO_3 by strong nitric acid.

Reactions in the Wet Way

Since nitric acid does not form characteristic insoluble salts, it cannot be detected by means of precipitation; its identification depends upon its oxidizing action. Great care must be exercised before deciding whether this acid is present, for other oxidizing substances give similar (in some cases the same) reactions.

1. **Dilute Sulfuric Acid** gives no reaction (difference from nitrous acid).

2. **Concentrated Sulfuric Acid** when heated with any nitrate causes evolution of yellowish brown vapors of NO_2, with a characteristic penetrating odor.

3. **Silver Nitrate** and **Barium Chloride** cause no precipitation.

4. **Brucine Reaction.** *Reagent.* — Dissolve 0.2 g of brucine in 100 ml of pure concentrated sulfuric acid.*

Procedure. — Mix the solution to be tested for nitric acid with three times its volume of pure, concentrated sulfuric acid, and add 1 ml of freshly prepared brucine solution. If nitric acid is present, a red coloration quickly appears, which rapidly changes to orange, then slowly to lemon or gold yellow, and finally becomes greenish yellow. Nitrous acid does not give this reaction provided it is present as "nitrose," *i.e.*, dissolved in concentrated sulfuric acid. Aqueous solutions of nitrites always yield a small amount of nitric acid when acidified with sulfuric acid, and consequently give the brucine reaction.

Sulfuric acid often contains a little nitric acid. If the concentrated acid is diluted to density 1.4 and boiled for some time in a platinum dish, all HNO_2 and HNO_3 can be removed.

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* Lunge, *Z. angew. Chemie*, **1894**, 348.

5. **Diphenylamine Reaction** (the Lunge test).* *Reagent.* — Dissolve 0.5 g of diphenylamine in 100 ml of pure, concentrated sulfuric acid diluted with 20 ml of water.

Procedure. — Place a few ml of the diphenylamine solution in a test tube and carefully cover it with the solution to be tested. If nitric acid is present, a ring of a beautiful blue color is formed at the zone of contact between the two liquids.

This very sensitive reaction is, unfortunately, also caused by nitrous, chloric, and selenic acids, ferric chloride, and many other oxidizing agents. Even fuming sulfuric acid will give it sometimes.

In the absence of ferric and selenic salts, it is useful for detecting the presence of small amounts of nitrogen acids in sulfuric acid. In this case first pour the concentrated sulfuric acid to be tested into the test tube and cover it with the specifically lighter diphenylamine solution. If 1 ml of an acid containing only $\frac{1}{20}$ mg of nitrogen in a liter is used, the reaction will cause a noticeable coloration. If very strong fuming sulfuric acid is to be tested, dilute it first with concentrated sulfuric acid until it does not contain more than 20 per cent excess SO_3.

6. **Ferrous Salts** are oxidized by nitric acid, which is itself reduced to nitric oxide, NO:

$$3\ Fe^{++} + NO_3^- + 4\ H^+ \rightarrow 3\ Fe^{+++} + 2\ H_2O + NO\uparrow$$

If the reaction takes place in the cold, the nitric oxide combines with the excess of ferrous salt, forming a dark brown, very unstable compound, *e.g.*, $FeSO_4 \cdot xNO$. This compound is decomposed, on warming, into ferrous salt and nitric oxide (which escapes), the brown color disappearing. If more than enough nitric acid is present to oxidize completely the ferrous salt to ferric salt, a more reddish coloration is obtained owing to the formation of a salt such as $Fe_2(SO_4)_3 \cdot 4\ NO$.

The test is best carried out in the following manner:

Place some of the substance to be tested for nitrate in a test tube with 5 ml of water, add an equal volume of concentrated sulfuric acid, and cool nearly to room temperature by shaking the solution under running water. Carefully add about 5 ml of saturated ferrous sulfate solution down the sides of the test tube so that it forms a layer on top of the concentrated sulfuric acid solution. When a nitrate is present a brown ring is formed at the zone of contact between the ferrous sulfate solution and the heavier sulfuric acid solution, or if considerable nitric acid is present the whole of the ferrous sulfate solution may be colored. If only a little nitric acid is present, the zone may be colored pink owing to the formation of $Fe_2(SO_4)_3 \cdot 4\ NO$. The test is not reliable in the presence of an iodide, chromate, cyanide, ferrocyanide, thiocyanate, sulfite, or thiosulfate. The test can be made on a spot plate.

Place a piece of ferrous sulfate about as large as a pinhead in one of the cavities of a spot plate. Add a drop of the solution to be tested and one of concentrated sulfuric acid; if 2.5 γ of nitrate is present, a brown ring will form around the crystal of ferrous sulfate.

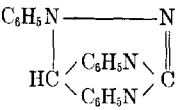
Nitrous acid gives the same reaction, with the difference that it takes place even without the addition of concentrated sulfuric acid.

7. **Indigo Solution** is decolorized by warming with nitric acid (as well as by other oxidizing agents).

* Lunge, *Z. angew. Chemie*, **1894**, 345.

8. **Manganous Chloride.** — A saturated solution of manganous chloride in concentrated hydrochloric acid gives a dark brownish black coloration with a nitrate owing to the formation of $MnCl_3$ in the solution. The reaction is caused by other oxidizing agents.

9. **Nitron Reaction.** — A 10 per cent solution of nitron (3-n-diphenyl-1, 4-endanilo-3, 4-dihydro-2, 3-triazole) in acetic acid gives a white precipitate of nitron nitrate. The reaction is not characteristic of nitrate ions, for the bromide, iodide, nitrite, chromate, chlorate-perchlorate, thiosulfide, ferrocyanide, ferricyanide, and picrate of nitron are insoluble compounds. The chemical formula of nitron is



As reagent, a 10 per cent solution in acetic acid is used.

10. **Potassium Iodide** is not decomposed by pure, dilute nitric acid (difference from nitrous acid).

If to the solution of a nitrate, some potassium iodide, a few drops of an acid (best acetic acid), and a little zinc are added, the nitric acid is reduced to nitrous acid, which then reacts with hydriodic acid and the solution becomes yellow on account of the liberation of iodine. By shaking the solution with carbon disulfide, the latter will be colored reddish violet, or the iodine may be detected by adding a little starch paste.

The reactions which take place may be represented by the following equations:

$$Zn + NO_3^- + 2\,H^+ \rightarrow Zn^{++} + NO_2^- + H_2O$$
$$2\,NO_2^- + 2\,I^- + 4\,H^+ \rightarrow 2\,NO\uparrow + 2\,H_2O + I_2$$

If it is desired to detect the free iodine by forming a solution in carbon disulfide, the latter *under no circumstances* should be added before the zinc has been allowed to act upon the acid solution of the nitrate and potassium iodide. In such a case, there will often be no separation of iodine, because zinc reduces the carbon disulfide to thioformaldehyde and hydrogen sulfide, and the latter reacts with any iodine which may be formed, changing it back to hydriodic acid:

$$CS_2 + 4\,H^+ + 2\,Zn \rightarrow 2\,Zn^{++} + CH_2S + H_2S$$
$$H_2S + I_2 \rightarrow 2\,HI + S$$

11. **Salicylic Acid** (2 g in 30 ml of concentrated sulfuric acid) gives a yellow coloration when heated with a solid nitrate, nitro-salicylic acid being formed.

12. **Zinc** or **Aluminum in Alkaline Solutions** and **Devarda's alloy** reduce nitrates:

$$3\,NO_3^- + 8\,Al + 5\,OH^- + 2\,H_2O \rightarrow 8\,AlO_2^- + 3\,NH_3\uparrow$$

If a nitrate solution is boiled with zinc dust and an alkali, a considerable evolution of ammonia takes place:

$$NO_3^- + 4\ Zn + 7\ OH^- \rightarrow 4\ ZnO_2^{--} + 2\ H_2O + NH_3\uparrow$$

This reaction is particularly suited for the detection of nitric acid in the presence of chloric acid (cf. p. 424).

The test for nitric acid can be based on the formation of nitrous acid which gives a red coloration with sulfanilic acid and α-naphthylamine.

Place 1 drop of the neutral or acetic acid solution on a spot plate; mix with 1 drop of 1 per cent sulfanilic acid, $C_6H_4(SO_3H)NH_2$, in 30 per cent acetic acid and 1 drop of 0.3 per cent α-naphthylamine in 30 per cent acetic acid. Add a few milligrams of zinc, and a red coloration results with 0.05 γ of HNO_3. The dyestuff $C_6H_4(SO_3H) \cdot N_2C_{10}H_6(NH_2)$ is formed.

DETECTION OF NITRIC ACID IN THE PRESENCE OF NITROUS ACID

There is no absolutely reliable qualitative test for the detection of traces of nitric acid in the presence of large amounts of nitrous acid in aqueous solution. A number of methods have been proposed which depend upon the destruction of the nitrous acid by diazotizing, but they all yield only approximate results because, in order to destroy the nitrous acid, it is necessary first to set the acid itself free by the addition of another acid, which always causes a part of the nitrous acid to be changed to nitric acid; so that the latter will be detected even when no nitric acid was originally present.

Large amounts of nitric acid in the presence of nitrous acid may be detected by the method proposed by Piccini,* in which a concentrated solution containing salts of both acids is treated with a concentrated solution of urea, and then covered (by means of a pipet) with dilute sulfuric acid. A lively evolution of nitrogen and carbon dioxide ensues, which ceases in a few minutes:

$$\underset{\text{Urea}}{CO(NH_2)_2} + 2\ HNO_2 \rightarrow CO_2\uparrow + 3\ H_2O + 2\ N_2\uparrow$$

When the evolution of gas has ceased, test the solution for nitric acid by means of the diphenylamine reaction.

This reaction, however, does not take place quickly enough to prevent traces of nitric acid being formed according to the following equation:

$$3\ HNO_2 \rightarrow H_2O + HNO_3 + 2\ NO\uparrow$$

The odor of nitrous fumes is always perceptible in the escaping nitrogen;† the presence of nitrous acid in the fumes can also usually be detected by means of iodo-starch paper. The nitric acid which remains in the solution can be detected by means of the diphenylamine reaction.

If the diphenylamine reaction gives a very intense coloration after the destruction of the nitrous acid by means of urea, the presence of nitric acid in the original compound is assured; but if the reaction shows that only a trace of nitric acid is present it is probably due simply to small amounts of nitric acid formed by the destruction of the nitrous acid.

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* *Z. anal. Chem.*, **19**, 354 (1880).

† Even at 0° and in an atmosphere of carbon dioxide.

The nitrous acid may also be destroyed by boiling an alkaline nitrite solution with neutral ammonium chloride; but traces of nitric acid are always formed at the same time.*

Probably the two most satisfactory methods of removing nitrous acid prior to making the test for nitric acid are the reactions with sodium azide, NaN_3, and with aminosulfonic acid, $NH_2 \cdot SO_3H$:

$$NaN_3 + HNO_2 \rightarrow N_2 + N_2O\uparrow + NaOH$$
$$HNO_2 + NH_2 \cdot SO_3H \rightarrow H_2SO_4 + H_2O + N_2\uparrow$$

In the first method, add some sodium azide to a little of the solution to be tested, acidify, and after a little while heat to boiling. For the second method, use a little of the test solution and mix with 0.5 per cent aminosulfonic acid; the reaction is so violent with concentrated solutions that some HNO_3 is likely to be formed by oxidation of the HNO_2.

Reactions in the Dry Way

By ignition, nitrates of the alkalies are changed into nitrites with loss of oxygen, and the nitrites are decomposed on stronger ignition into oxide:

$$2\ KNO_3 \rightarrow 2\ KNO_2 + O_2\uparrow$$
$$4\ KNO_2 \rightarrow 2\ K_2O + 4\ NO\uparrow + O_2\uparrow$$

All nitrates deflagrate on being heated on charcoal, *i.e.*, the charcoal burns at the expense of the oxygen of the nitric acid, with vivid scintillation.

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* By evaporating with ammonium carbonate solution the decomposition scarcely takes place at all.

CHLORIC ACID, $HClO_3$

Properties. — Chlorates are formed by conducting chlorine into hot alkali hydroxide or alkaline earth hydroxide solution (not NH_4OH), by the electrolysis of a hot chloride solution, or by the oxidation of hypochlorites.

Free chloric acid is unstable and is decomposed at 40° into perchloric acid with loss of chlorine and oxygen (cf. p. 228):

$$3\ HClO_3 \rightarrow H_2O + 2\ ClO_2\uparrow + HClO_4$$

and

$$2\ ClO_2 \rightarrow Cl_2\uparrow + 2\ O_2\uparrow$$

The aqueous solution of chloric acid behaves as a strong acid; in 0.5 normal solution it is 88 per cent ionized. By evaporation in a vacuum, the aqueous solution can be concentrated until its density is about 1.28, when it corresponds to $HClO_3 \cdot 7\ H_2O$ with 40.1 per cent $HClO_3$. This is fairly stable but decomposes slowly with liberation of Cl_2 and O_2; $3\ HClO_3 \rightarrow HClO_4 + 2\ O_2 + Cl_2 + H_2O$.

The following three equations also represent ways in which $HClO_3$ can decompose:

$$4\ HClO_3 \rightarrow 3\ HClO_4 + HCl$$
$$2\ HClO_3 \rightarrow 2\ HCl + 3\ O_2$$
$$4\ HClO_3 \rightarrow 4\ ClO_2 + O_2 + 2\ H_2O$$

Chloric acid and its salts are strong oxidizing agents; potassium chlorate is used in matches, fireworks, and explosives. Chloric acid oxidizes oxalates to CO_2, HCNS to H_2SO_4 and HCN, phosphorus compounds of lower valence to H_3PO_4, sulfur compounds of lower valence to H_2SO_4, HCl to Cl_2, HBr to Br_2, and I_2 to KIO_3 and ICl_3. Magnesium dissolves in chloric acid to form $Mg(ClO_3)_2$ and H_2, but with zinc and dilute sulfuric acid the reduction of the ClO_3^- to Cl^- can be made complete. Manganous sulfate is not oxidized by $HClO_3$ alone, but with concentrated nitric acid, black hydrated MnO_2, and with phosphoric acid violet $[Mn(PO_4)_2]^{---}$, can be formed.

Solubility. — All chlorates are soluble in water although the solid mercury, bismuth, and tin salts require a little acid to prevent hydrolysis. Mercurous and ferrous chlorates are very unstable. Potassium chlorate is the least soluble stable chlorate, and 100 ml of cold water will dissolve only 6.6 g of $KClO_3$ whereas the same quantity of water will dissolve 315 g of $LiClO_3$.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** sets free chloric acid from chlorates, which, as above stated, is gradually decomposed, with loss of chlorine and oxygen, into perchloric acid. The solution, therefore, acts as an oxidizing agent, particularly on warming; it will turn iodo-starch blue:

$$ClO_3^- + 6\ I^- + 6\ H^+ \rightarrow Cl^- + 3\ H_2O + 3\ I_2$$

The speed of the reaction between the chlorate and the iodide depends upon the concentration of the hydrogen ion. The salts do not react strongly as oxidizing agents in neutral solutions (difference from hypochlorites).

2. **Concentrated Sulfuric Acid** decomposes all chlorates, setting free greenish yellow chlorine dioxide gas, which colors the sulfuric acid yellow and explodes violently on warming:

$$3\ KClO_3 + 3\ H_2SO_4 \rightarrow 3\ KHSO_4 + HClO_4 + 2\ ClO_2\uparrow + H_2O$$

A very small crystal of chlorate added to 1 ml of concentrated sulfuric acid on a watch glass will color the acid and give a chlorine-like odor.

3. **Silver Nitrate** and **Barium Chloride** do not cause precipitation.

4. **Aniline Sulfate Test.** — Add a little of the solid to be tested to about 1 ml of concentrated sulfuric acid and introduce one or two drops of an aqueous aniline sulfate solution; a deep blue color is obtained with a chlorate but not with a nitrate.

5. **Diphenylamine** reacts the same as with nitric acid.

6. **Ferrous Salts.** — By boiling chlorates with ferrous salts in the presence of dilute acid, the chlorate is quickly reduced to chloride (difference from perchloric acid):

$$ClO_3^- + 6\ Fe^{++} + 6\ H^+ \rightarrow 3\ H_2O + Cl^- + 6\ Fe^{+++}$$

7. **Concentrated Hydrochloric Acid** decomposes all chlorates; the acid is colored yellow and chlorine is evolved:

$$ClO_3^- + 5\ Cl^- + 6\ H^+ \rightarrow 3\ H_2O + 3\ Cl_2\uparrow$$

This equation is not quite correct, for some ClO_2 is always mixed with the Cl_2. The following equation expresses this:

$$3\ ClO_3^- + 7\ Cl^- + 10\ H^+ \rightarrow 5\ H_2O + 4\ Cl_2\uparrow + 2\ ClO_2\uparrow$$

The proportion of ClO_2 and Cl_2 formed is influenced by the concentration of the reacting substances and the temperature.

If the hydrochloric acid is colored blue with indigo it will be decolorized by the free chlorine.

8. **Indigo Test.** — To the chlorate solution add enough indigo, dissolved in concentrated sulfuric acid, to give a light blue color. Add a little dilute sulfuric acid and introduce drop by drop a little sulfurous acid or sodium sulfite solution. The blue color will disappear quickly. The sulfurous acid reacts with the chlorate to form chlorine or hypochlorite and the chlorine or hypochlorite oxidizes the indigo. The test is sensitive.

9. **Manganous Chloride** in concentrated hydrochloric acid is darkened by chloric acid. This test merely shows that an oxidizer is present.

10. **Manganese Sulfate** in concentrated phosphoric acid gives, on heating, a purple colored manganiphosphate ion:

$$ClO_3^- + 6\ Mn^{++} + 12\ H_3PO_4 \rightarrow 6\ [Mn(PO_4)_2]^{---} + Cl^- + 30\ H^+ + 3\ H_2O$$

Persulfates and periodiates give the same test. The former can be decomposed by evaporating the sulfuric acid solution with a little silver nitrate as catalyst:

$$2\,H_2S_2O_8 + 2\,H_2O \rightarrow 4\,H_2SO_4 + O_2.$$

Place a drop of the solution to be tested together with a drop of saturated manganese sulfate solution in a porcelain capsule and add a drop of sirupy phosphoric acid. Heat gently, and a violet coloration will appear. If the coloration is very slight, it can be intensified by adding a drop of 1 per cent diphenylcarbazide in alcohol; the carbazide is oxidized to a violet product.

11. **Reducing Agents** reduce chlorates to chlorides in acid and alkaline solutions.

The reduction in acid solution is effected by means of zinc and dilute sulfuric acid, sulfurous acid, or sodium nitrite:

$$3\,Zn + ClO_3^- + 6\,H^+ \rightarrow 3\,Zn^{++} + Cl^- + 3\,H_2O$$
$$3\,SO_3^{--} + ClO_3^- \rightarrow Cl^- + 3\,SO_4^{--}$$
$$3\,NO_2^- + ClO_3^- \rightarrow 3\,NO_3^- + Cl^-$$

The reduction in alkaline or neutral * solution is brought about by boiling the solution with zinc dust, aluminum powder, Devarda's alloy (cf. p. 37), or a copper-zinc couple:†

$$ClO_3^- + 3\,Zn + 6\,OH^- \rightarrow 3\,ZnO_2^{--} + Cl^- + 3\,H_2O$$

The residual metal is filtered off, the solution acidified with nitric acid,‡ and silver nitrate added, when the characteristic, curdy precipitate of silver chloride is formed.

SPECIAL PROCEDURES FOR CHLORATES

Test for Hypochlorite in Chlorates

To test for the presence of hypochlorite in an alkali chlorate, dissolve about 2 g of the salt in 200 ml of water, add 3 ml of 10 per cent KI solution and 3 ml of starch solution, but *no sulfuric acid;* the solution will at once turn blue if a trace of hypochlorite is present. As little as 0.1 mg of hypochlorite will give the test.

Detection of Hydrochloric, Nitric, and Chloric Acids in the Presence of One Another

Procedure I.— First, test for the presence of chloride anions by treating a part of the solution with silver nitrate; a white precipitate of silver chloride shows the presence of hydrochloric acid. Treat the remainder of the solution with silver sulfate solution until no further precipitation of silver chloride takes place, and filter off the precipitate.

Boil the filtrate with a little caustic potash (in order to expel any ammonia from ammonium salts which may be present), add zinc dust (or Devarda's alloy), and again boil; if nitric acid is present, ammonia will be given off. Filter off the residue, acidify the filtrate with nitric acid, and treat with silver nitrate. If a precipitate of silver chloride is now obtained, chloric acid was originally present.

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* The reaction takes place very slowly in neutral solutions.

† Treat granulated zinc with 1 per cent copper sulfate solution, wash, and dry the residue.

‡ On acidifying with nitric acid a heavy precipitate of $Zn(OH)_2$ is obtained which dissolves in more nitric acid.

Procedure II. — Test a small part of the solution for hydrochloric acid by adding silver nitrate in excess, filter off the precipitate, treat the filtrate with sulfurous acid, and again test with silver nitrate: a precipitate of silver chloride shows the presence of chloric acid. Enough nitric acid must be added to dissolve any silver sulfite that may form.

Test a second portion of the solution, as above, for nitric acid.

Reactions in the Dry Way

On ignition, all chlorates are decomposed, forming a chloride with loss of oxygen. By heating on charcoal, deflagration takes place.

PERCHLORIC ACID, $HClO_4$

Preparation. — Perchloric acid is the most stable of the acids containing chlorine and oxygen. It can be obtained by evaporating a solution of chloric acid and has been prepared by distilling potassium perchlorate with concentrated sulfuric acid. In this way the solid, crystalline monohydrate, $HClO_4 \cdot H_2O$, is formed which upon further heating is decomposed at 110° into the oily dihydrate and $HClO_4$ which distils off. At 203° the dihydrate distils.

With the exception of potassium perchlorate, which occurs as a minor ingredient of Chile saltpeter, $NaNO_3$, the most common salt of perchloric acid is ammonium perchlorate, which is easily made from sodium perchlorate, a by-product in the electrolytic manufacture of sodium chlorate. If ammonium perchlorate is treated with hot, dilute hydrochloric acid and some nitric acid, the NH_4^+ is oxidized to N_2O and a dilute solution of $HClO_4$ is obtained. If this solution is evaporated until the temperature is 180–200° all the nitric and hydrochloric acid will be removed, and then, by distilling in a vacuum (2–7 mm) a 70–73.6 per cent solution of perchloric acid is obtained. This is the safest way to make perchloric acid.

Properties. — Anhydrous perchloric acid has a freezing point of approximately −112°, and its boiling point is about 130°. Anhydrous perchloric acid is very dangerous. If it is prepared by distilling in a vacuum and is then allowed to stand at room temperature, it gradually assumes a straw color, then turns brown, and finally explodes. The decomposition is probably accelerated by photochemical synthesis of colored reduction products which are unstable. Contact with bits of charcoal, wood, paper, or dust often causes an explosion. Concentrated perchloric acid produces very painful wounds that are slow to heal.

At very low temperatures the anhydrous acid will keep indefinitely. Hot, concentrated perchloric acid is a powerful dehydrating agent, like sulfuric acid, and also an excellent oxidizing agent. In fact, hot, concentrated perchloric acid is almost as good an oxidizer as a mixture of chromic acid and sulfuric acid, but the perchloric acid loses its oxidizing power as soon as it is cold. Perchloric acid is a valuable reagent. It is used as a test for potassium in qualitative analysis, as a solvent, and as an oxidizing agent. Potassium perchlorate has, to some extent, replaced potassium chlorate in fireworks; magnesium perchlorate is sold under the name *anhydrone* as a dehydrating agent, and barium perchlorate has been sold for the same purpose under the name *desicchlora*.

The salts of this monobasic acid, the perchlorates, are remarkably stable; they contain chlorine with seven positive charges and are isomorphous with the permanganates. The potassium salt is obtained from potassium chlorate. On melting the latter compound, at first a lively stream of oxygen is given off which, however, soon lessens. The melt quickly becomes viscous, and consists of potassium chloride and potassium perchlorate,

$$2\,KClO_3 \rightarrow KCl + KClO_4 + O_2\uparrow$$

and the latter may be separated from the much more soluble potassium chloride by recrystallization.

Solubility. — All perchlorates except the ammonium, potassium, rubidium, and cesium salts are easily soluble in water. The difficultly soluble alkali salts are dissolved by hot water, but the precipitation of the potassium, rubidium, and cesium salts is practically complete when an equal volume of alcohol is added to the cold saturated solution.

Reactions in the Wet Way

Perchloric acid is not attacked by concentrated sulfuric acid, nor is it reduced to chloride by zinc dust, Devarda's alloy, sulfurous acid, or acid solutions of ferrous salts.

1. **Potassium Salts** precipitate the relatively insoluble, white, crystalline $KClO_4$ (cf. p. 282) insoluble in alcohol. Ammonium salts give a similar precipitate.

2. **Silver Nitrate** and **Barium Chloride** produce no precipitation.

3. **Titanium Trichloride,** $TiCl_3$, **Hyposulfurous Acid,** $H_2S_2O_4$, and the lower oxidation products of vanadium, molybdenum, and tungsten reduce perchlorates to chlorides.

Reactions in the Dry Way

The perchlorates deflagrate on being heated on charcoal; on fusing they lose oxygen, leaving chloride behind, which when dissolved in water gives all the reactions for hydrochloric acid. If a perchlorate is fused with a chloride, *e.g.*, zinc chloride, chlorine is evolved. If the chlorine is driven over, by a stream of carbon dioxide, into potassium iodide solution, iodine is set free. If nitrates are present, they can be decomposed first by evaporating to dryness with concentrated hydrochloric acid, and then, to make sure that no traces of nitrate remain, Gooch and Kreider recommend evaporating with manganous chloride and concentrated hydrochloric acid, and again evaporating with hydrochloric acid. Finally they precipitate the manganese with sodium carbonate, filter, and evaporate the filtrate to dryness, and then test the residue for perchlorate by fusing with zinc chloride.

It is sometimes desirable to remove perchloric acid from a solution to be analyzed for the alkali metals. This is best accomplished by evaporating to dryness and igniting with ammonium salt:

$$3\ NaClO_4 + 8\ NH_4Cl \rightarrow 3\ NaCl + 4\ N_2\uparrow + 8\ HCl\uparrow + 12\ H_2O\uparrow.$$

PERSULFURIC ACID, $H_2S_2O_8$

Preparation. — Pure persulfuric acid itself has never been isolated, its solution in sulfuric acid alone being known. It was first prepared by M. Marshall,* who electrolyzed fairly dilute sulfuric acid, keeping it very cold. During the electrolysis hydrogen ions are discharged at the cathode and unite to form hydrogen molecules, while HSO_4^- anions are discharged at the anode and unite to form persulfuric acid:

$$2\,H_2SO_4 \rightarrow H_2 + H_2S_2O_8$$

The preparation of ammonium persulfate, from which all other persulfates are made, is entirely analogous.

The anhydride, S_2O_7, was first obtained by Berthelot as a result of the action of a silent electric discharge upon a mixture of dry SO_2 and oxygen. At 0° it exists as flexible crystalline needles which are fairly stable but decompose slowly into SO_3 and O_2. The solution in water hydrolyzes and permonosulfuric acid (Caro's acid), H_2SO_5, is formed which, in turn, decomposes into H_2SO_4 and H_2O_2.

$$S_2O_7 + H_2O \rightarrow H_2S_2O_8$$
$$H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5$$
$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2$$

A mixture of sulfuric and perchloric acid is often used to destroy organic matter when it is desired to detect the presence of inorganic constituents.

The most important salts of persulfuric acid are those of ammonium, potassium, and barium. $(NH_4)_2S_2O_8$ is readily soluble in water, and forms monoclinic crystals; $K_2S_2O_8$ is difficultly soluble in cold water, but much more soluble in hot water, from which solution it is obtained by rapid cooling in the form of long crystals; $BaS_2O_8 + 4\,H_2O$ is made by triturating ammonium persulfate with barium hydroxide, and is fairly soluble in water.

Persulfates are powerful oxidants, and the potassium and ammonium salts are much used in chemical analysis. Under suitable conditions they oxidize Fe^{++} to Fe^{+++}, Cr^{+++} to $Cr_2O_7^{--}$, Ti^{+++} to Ti^{++++}, Co^{++} to Co^{+++}, Ni^{++} to Ni^{+++}, Mn^{++} to MnO_2 or MnO_4^- (in the presence of Ag^+), Ce^{+++} to Ce^{++++}, etc. Halides are oxidized to free halogen by persulfates or to a salt of a halogen oxy-acid if Ag^+ is present.

When a solution of alkali persulfate is boiled, oxygen gas is evolved and a normal sulfate is formed;

$$2K_2S_2O_8 + 2H_2O = 2K_2SO_4 + 2H_2SO_4 + O_2$$

When potassium persulfate is dissolved in concentrated sulfuric acid, permonosulfuric acid, H_2SO_5, (cf. p. 431) is formed.

Reactions in the Wet Way

A solution of ammonium persulfate can be used.

1. Water. — All persulfates are decomposed in aqueous solution (slowly in the cold, but more quickly on warming), forming sulfate,

* *J. Chem. Soc.*, **59**, 771.

free sulfuric acid, and oxygen:

$$2\,S_2O_8^{--} + 2\,H_2O \rightarrow 4\,HSO_4^- + O_2\uparrow$$
$$2\,BaS_2O_8 + 2\,H_2O \rightarrow 2\,BaSO_4 + 2\,H_2SO_4 + O_2\uparrow$$

A large proportion of the oxygen escapes as ozone, which can be detected by its odor or by its property of turning iodo-starch paper blue. A dilute solution of ammonium persulfate decomposes slowly at 20° C, without evolution of oxygen, part of the nitrogen being oxidized to nitric acid:

$$4\,(NH_4)_2S_2O_8 + 3\,H_2O \rightarrow 7\,(NH_4)HSO_4 + H_2SO_4 + HNO_3$$

2. **Dilute Sulfuric Acid** acts the same as water.

3. **Concentrated Sulfuric Acid.** — If a solid persulfate is dissolved in concentrated sulfuric acid at 0° C, a liquid is obtained which possesses very strong oxidizing properties. The mixture is known as Caro's acid.* For further particulars concerning this acid see page 431.

4. **Silver Nitrate** precipitates black silver peroxide:

$$2\,Ag^+ + S_2O_8^{--} + 2\,H_2O \rightarrow 2\,HSO_4^- + 2\,H^+ + \mathbf{Ag_2O_2}$$

If, however, the concentrated solution of ammonium persulfate is treated with ammonia and a very little silver nitrate, a lively evolution of nitrogen takes place, and the solution becomes heated to boiling. Silver peroxide is formed first, and oxidizes the ammonia to water, setting free nitrogen (catalysis).†

5. **Barium Chloride** does not give a precipitate immediately in a freshly prepared, cold solution of a persulfate; but, on standing some time, or on boiling, insoluble barium sulfate is precipitated.

6. **Manganese, Cobalt, Nickel,** and **Lead Salts** are oxidized in the presence of alkali to black peroxides:

$$Mn^{++} + S_2O_8^{--} + 4\,OH^- \rightarrow 2\,SO_4^{--} + \mathbf{H_2MnO_3} + H_2O$$

In this last reaction persulfuric acid reacts exactly similarly to hydrogen peroxide. It may be distinguished, however, by the fact that it does not decolorize a solution of potassium permanganate, does not produce a yellow coloration with titanium sulfate, and does not react with chromic acid to form chromium peroxide (cf. p. 202). Ferrous salts are readily oxidized to ferric salts, and cerous salts are changed to yellow ceric salts by persulfates, but the latter are not decolorized by an excess of the persulfate, while they are by hydrogen peroxide.

Manganese and lead salts are precipitated quantitatively from neutral and slightly acid solutions by alkali persulfates, cobalt incompletely from neutral solutions and

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* *Z. angew. Chem.*, **1898**, 845; *Ber.*, **34**, 853 (1901); *Ber.*, **41**, 1839 (1909).

† *Z. physik. Chem.*, **37**, 255 (1901).

not at all from acid ones, and nickel only in the presence of alkali. Hydrogen peroxide produces precipitates of peroxides in all these solutions only in the presence of alkali. In the presence of silver ions, which have a catalytic effect, manganous ions are oxidized to permanganate in hot nitric acid solutions by means of alkali persulfates.

$$5\,S_2O_8^{--} + 2\,Mn^{++} + 8\,H_2O \rightarrow 2\,HMnO_4 + 10\,SO_4^{--} + 14\,H^+$$

7. **Potassium Iodide** reacts with neutral solutions of persulfate and iodine is liberated:

$$2\,I^- + S_2O_8^{--} \rightarrow 2\,SO_4^{--} + I_2$$

Percarbonates and perborates do not give this reaction.

MONOPERSULFURIC ACID (CARO'S ACID) H_2SO_5

This acid is formed by the hydrolysis of persulfuric acid,

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5$$

and by the action of perhydrol (30 per cent hydrogen peroxide) on sulfuric acid:

$$H_2SO_4 + H_2O_2 \rightarrow H_2O + H_2SO_5$$

Unlike hydrogen peroxide, it does not reduce permanganates and it causes the liberation of iodine from potassium iodide solutions more readily than persulfates do:

$$H_2SO_5 + 2\,H^+ + 2\,I^- \rightarrow H_2SO_4 + H_2O + I_2$$

It is usually assumed that hydrogen peroxide, persulfuric acid, and monopersulfuric acid all contain an atom of oxygen directly connected to another atom of oxygen; this atom of oxygen, therefore, has a positive and a negative charge residing upon it (cf. p. 35).

GROUP VI

Silver Nitrate produces no precipitate.
Barium Chloride produces a white precipitate, insoluble in acids.

SULFURIC ACID, H_2SO_4

Preparation. — The sulfuric acid of commerce is made either by the lead-chamber or the contact process. The raw material in both processes is SO_2 obtained by burning sulfur or by roasting a sulfide such as pyrite, FeS_2. In the lead-chamber process, the SO_2 is oxidized by the action of nitrous anhydride and air to SO_3 which unites with water to form H_2SO_4. The contact process, which has to a large extent replaced the older lead-chamber process, is based upon the fact that the oxidation of SO_2 by the oxygen of the air is hastened by contact with substances such as pumice, porcelain, ferric oxide or finely divided platinum or vanadium pentoxide.

Properties. — Pure sulfuric acid at ordinary temperatures is a colorless, oily liquid of density 1.838; at low temperatures it is a solid which melts at 10.5°. If the acid is subjected to distillation, it is always partially decomposed; heavy, white vapors of SO_3 are given off first, and at 338° C a 98 per cent acid distils over. At a red heat, decomposition into H_2O, SO_2, and O_2 takes place. Ordinary commercial sulfuric acid has a density of 1.83-1.84, and contains 93-96 per cent H_2SO_4. The maximum density is reached when 97.35 per cent H_2SO_4 is present. Commercial sulfuric acid often contains lead sulfate, selenic acid, platinum, palladium, arsenious acid, the nitrogen acids, and small amounts of organic matter (whereby it is often colored brown) as impurities. Concentrated sulfuric acid is very hydroscopic, and is used for drying gases, etc.

The anhydride of sulfuric acid, SO_3, dissolves in concentrated sulfuric acid, forming pyrosulfuric acid, $H_2S_2O_7$, which is solid at ordinary temperatures, melts at 35°, and loses SO_3 at higher temperatures. It fumes strongly, and is called, therefore, *fuming sulfuric acid.* Pure, anhydrous H_2SO_4 cannot be made by evaporation or distillation but can be obtained by adding a slight excess of SO_3 to the 98 per cent acid and passing dry air through the acid until the excess SO_3 is removed. *Pyrosulfuric acid*, $H_2S_2O_7$, often called *Nordhausen acid* or *oleum*, is made by dissolving the necessary quantity of SO_3 in concentrated H_2SO_4. It forms crystals melting at 35°. Commercial oleum is equivalent to about 80 per cent H_2SO_4 plus 20 per cent SO_3, and the total SO_3 content is equivalent to 104.5 per cent H_2SO_4; in other words, the excess SO_3 in 100 g of oleum will unite with 4.5 g of water to form 100 per cent H_2SO_4. Sulfuric acid is dibasic and forms both neutral and acid salts.

Sulfuric acid is a strong acid and when evaporated with less volatile acids, or with a solution of their salts, does not begin to fume until these acids are expelled practically completely. At temperatures much below the boiling point, *e.g.*, at 160°, the formation of heavy, white fumes which produce a choking sensation in the throat and cause coughing is often taken as evidence that the more volatile mineral acid

have all been expelled and, for this reason, analytical procedures often call for "evaporation until dense fumes are evolved." Sulfuric acid is displaced from its salts by heating above its boiling point with the less volatile phosphoric, boric, and silicic acids.

Sulfuric acid is miscible with water in all proportions; considerable heat is evolved, and great care should be taken, in diluting sulfuric acid with water. The acid should be cold and the water must be added very slowly. It is always best to pour the acid very slowly into water and avoid, as far as possible, the reverse operation. After the acid has been mixed with an equal volume of water, there is no further danger of spattering. Sulfuric acid is a strong dehydrating agent and is often used for drying gases or for absorbing water vapor — hence its use in desiccators and in drying tubes. It also removes water from organic compounds and thereby often causes charring.

Solubility. — Most sulfates are soluble in water; calcium sulfate is difficultly soluble, strontium and lead sulfates are very difficultly soluble, and barium sulfate is practically insoluble in water. There are also a number of basic sulfates, Hg, Bi, Cr, which are insoluble in water, but are, as a rule, easily dissolved by dilute acid.

Reactions in the Wet Way

1. **Barium Chloride** precipitates, from even the most dilute solutions, white barium sulfate, insoluble in acids.

2. **Silver Nitrate** causes no precipitation in dilute solutions, but in concentrated solutions a white, crystalline precipitate is formed (100 ml of water dissolve at 18° C only 0.58 g of silver sulfate).

3. **Lead Acetate** precipitates white lead sulfate, soluble in concentrated sulfuric acid, ammonium acetate, and ammonium tartrate solutions (cf. p. 115).

To detect the presence of SO_4 in insoluble sulfates, treat with sodium carbonate, whereby insoluble carbonate and soluble sodium sulfate are formed.

Lead sulfate and calcium sulfate are easily decomposed by *boiling* with sodium carbonate solution, but barium and strontium sulfates are only incompletely decomposed by this treatment; they are much more readily attacked by *fusing* with four times as much sodium carbonate (cf. p. 268). Even barium sulfate, however, is decomposed sufficiently for the purposes of qualitative analysis by *boiling* with sodium carbonate.

4. **Metals** in acid solution do not reduce the sulfates.

5. **Sodium Rhodizonate,** $\begin{matrix} CO-CO-C-O\cdot Na \\ | \quad\quad\quad\quad \| \quad\quad \\ CO-CO-C-O\cdot Na \end{matrix}$, gives a red precipitate with barium ions, but the red precipitate is decomposed by contact with sulfate ions and the precipitate becomes colorless.

Place a drop of freshly prepared, 5 per cent sodium rhodizonate upon filter paper and add to it a drop of barium chloride solution. A red spot will form, and the red color will disappear on adding a drop of an acid or alkaline solution containing SO_4^{--}.

Reactions in the Dry Way

The neutral salts of the alkalies melt with difficulty without being decomposed, while the acid salts of the alkalies readily give off water and SO_3 (cf. p. 193).

The sulfates of the alkaline earths and of lead do not undergo decomposition on ordinary ignition; the remaining sulfates are more or less decomposed.

All sulfates are reduced to sodium sulfide when heated with sodium carbonate on charcoal; if the product is placed upon a bright silver coin and moistened, a black stain of silver sulfide results, *e.g.*:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

$$Na_2SO_4 + 2\,C \rightarrow 2\,CO_2\uparrow + Na_2S$$

$$2\,Na_2S + 4\,Ag + 2\,H_2O + O_2 \rightarrow 4\,NaOH + 2\,\mathbf{Ag_2S}$$

This reaction is called the hepar reaction and is obtained with all substances that contain sulfur.

A very sensitive test for sulfate useful in the absence of other compounds containing sulfur consists in heating the sample in a capillary tube with a little metallic potassium whereby potassium sulfide is formed. Then, if the melt is dissolved in water, the sulfide present can be detected by the nitroprusside test (p. 353) or by the sodium azide test (p. 353).

HYDROFLUORIC ACID, H_2F_2 (or HF)

Occurrence. — Hydrofluoric acid occurs in nature only in the form of fluorides, of which the most important is fluorite, CaF_2, crystallizing in the isometric system. It is also found as cryolite, $Na_3[AlF_6]$, in Greenland, and in many silicates, such as tourmaline, topaz, lepidolite, apophyllite, apatite, etc.

Preparation. — Hydrofluoric acid is obtained by decomposing a fluoride with concentrated sulfuric acid in platinum or lead retorts:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + H_2F_2\uparrow$$

Properties. — Hydrofluoric acid at temperatures above 20° C is a colorless, exceedingly corrosive gas which changes at 19.4° C to a mobile, fuming liquid. Below −83°, it is solid. In the liquid state at 0°, its dielectric constant is higher than that of water. The vapors possess a penetrating odor and are poisonous. When in contact with the skin, the acid produces painful burns. On heating the concentrated aqueous solution, the gas H_2F_2 at first distils and then the 38.2 per cent acid, which has a constant boiling point. The acid is bimolecular, corresponding to the formula H_2F_2 up to +40°, but above +80° it is monomolecular. Between these temperatures, both HF and H_2F_2 molecules are present. In dilute aqueous solutions, the simple molecules preponderate, but in concentrated solutions at room temperature, there is considerable H_2F_2.

Hydrofluoric acid is distinguished from all other acids by its ability to dissolve silicic acid, a property which is utilized technically for etching glass, and in the analytical laboratory for detecting fluorine and silicic acid, as well as for decomposing silicates. On account of this action upon glass the acid must be kept in platinum, wax, or hard rubber, and prepared in platinum or lead vessels.

The action of hydrofluoric acid upon silicic acid takes place according to the equation

$$SiO_2 + 2\ H_2F_2 \rightarrow 2\ H_2O + SiF_4\uparrow$$

The velocity of the reaction depends upon the fineness and nature of the material. Thus Mackintosh* found after one hour's action of an excess of 9 per cent hydrofluoric acid upon quartz and opal powder that the quartz had lost only 1.56 per cent of its original weight while the opal had lost 77.28 per cent.

If precipitated and ignited silica is treated with strong hydrofluoric acid, it dissolves almost immediately with hissing and strong evolution of heat, while quartz powder under the same treatment is dissolved only slowly.

Most silicates, with regard to the ease with which they are attacked by hydrofluoric acid, stand intermediate between the precipitated silica and quartz, although some silicates are attacked more difficultly than quartz, and a few are only slightly acted upon.

Hydrofluoric acid, HF, in dilute aqueous solutions is a weak, monobasic acid having, in common with other weak acids like carbonic acid, acetic acid, etc., the property of turning blue litmus red and Brazil-wood paper yellow. The ionization constant is about 7.2×10^{-4} and in 0.1 normal solution it is about 10 per cent ionized. In

* *Chem. News*, **54**, 102.

concentrated solutions, hydrofluoride ions are formed,

$$HF + F^- \rightarrow HF_2^-$$

and the primary ionization of the dibasic H_2F_2 is considerably greater than that of the simpler molecules. The aqueous solution of an alkali fluoride has a strong alkaline reaction.

The property of forming very stable complex metal-hydrofluoric acids is characteristic of hydrofluoric acid as of hydrocyanic acid. Thus $H[AgF_2]$, $H[KF_2]$, $H[NaF_2]$, and $H[NH_4F_2]$ and the salts $Na_3[FeF_6]$, $Na_3[AlF_6]$, etc., are known.

Unlike the complex cyanogen compounds, of which the free acids either do not exist at all or represent very unstable compounds, the corresponding fluorine acids are fairly stable. Thus fluorargentic acid, $H[AgF_2]$, decomposes only on gentle heating into silver fluoride and hydrofluoric acid, and the corresponding alkali compounds are decomposed only upon ignition; for this reason the latter are suitable for attacking difficultly decomposable silicates, zircon, and titanium minerals, etc., which are only partially attacked by free hydrofluoric acid.

The relationship between hydrofluoric and hydrochloric acid is much less noticeable than that between hydrochloric acid and hydrobromic acid. Although fluorine is the lightest halogen, hydrofluoric acid has much the highest boiling point and is a liquid at temperatures where all the other halogen hydrides are gases. The other halogen hydrides are oxidized easily, but hydrofluoric acid is hard to oxidize and the oxygen acids, corresponding to hypochlorous, chlorous, chloric, and perchloric acids are not known.

Solubility. — The fluorides of the alkalies, of silver, aluminum, tin, and mercury are soluble in water; those of the alkaline earths, of lead, copper, and zinc, are insoluble, or at least very difficultly soluble. Silver fluoride is very soluble in water, and the solid salt deliquesces in damp air. This difference in the solubility of alkaline earth and silver salts as compared with the corresponding salts of hydrochloric, hydrobromic, and hydriodic acid is very characteristic.

Reactions in the Wet Way

For reactions 1, 2, and 3 use powdered calcium fluoride, but for reactions 4, 5, 6, and 7 use a solution of sodium fluoride.

1. **Dilute Sulfuric Acid** causes only a slight reaction.

2. **Concentrated Sulfuric Acid** reacts readily on warming, setting free hydrofluoric acid:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + H_2F_2\uparrow$$

Acid containing about 90 per cent H_2SO_4 is most suitable for this reaction. Acid containing an excess of SO_3 is likely to cause the formation of difficultly volatile fluorsulfonic acid, HSO_3F.

If the reaction is performed in a test tube, the hydrofluoric acid will attack the glass, forming volatile silicon fluoride and salts of hydrofluosilicic acid; but the latter are decomposed by the concentrated sulfuric acid into sulfate, hydrofluoric acid, and silicon fluoride,

$$\underset{\text{Soda glass}}{Na_2CaSi_6O_{14}} + 14\,H_2F_2 \rightarrow 14\,H_2O\uparrow + Na_2SiF_6 + CaSiF_6 + 4\,SiF_4\uparrow$$

and

$$Na_2SiF_6 + H_2SO_4 \rightarrow Na_2SO_4 + H_2F_2\uparrow + SiF_4\uparrow$$
$$CaSiF_6 + H_2SO_4 \rightarrow CaSO_4 + H_2F_2\uparrow + SiF_4\uparrow$$

The silicon fluoride formed by this reaction is a colorless gas with a penetrating odor, and is decomposed by water, forming gelatinous silicic acid and hydrofluoric acid:

$$(1)\ SiF_4 + 4\,H_2O \rightarrow H_4SiO_4 + 2\,H_2F_2\uparrow$$

Silicon fluoride, however, readily combines with hydrofluoric acid to form fluorosilicic acid,

$$(2)\ SiF_4 + H_2F_2 \rightarrow H_2[SiF_6]$$

which is not decomposed by water. The entire reaction, therefore, which takes place between silicon tetrafluoride and water is expressed by the sum of these last two equations, as follows:

$$3\,SiF_4 + 4\,H_2O \rightarrow \mathbf{H_4SiO_4} + 2\,H_2[SiF_6]$$

If, therefore, a fluoride be heated in a glass test tube with concentrated sulfuric acid, and the escaping vapors allowed to act upon water by placing a moist glass rod in the tube, the water adhering to the rod will become turbid.

Remark. — Although the above test rarely fails when relatively large amounts of fluoride are used, it will not be obtained in the case of certain minerals containing fluorine, such as topaz, tourmaline, etc. The test may fail, furthermore, if the fluoride is mixed with a large excess of that modification of silicic acid which is most readily attacked by hydrofluoric acid. According to Daniel,* this is due to the formation of a stable oxyfluoride, probably of the formula $SiOF_2$.

The silicon tetrafluoride at first formed combines with the excess of amorphous silicic acid present, as follows,

$$SiF_4 + SiO_2 \rightarrow 2\,SiOF_2$$

but this reaction will take place only very slowly, if at all, with quartz powder or with the silica of a silicate such as glass.

A positive result will be obtained invariably when the tetrafluoride test is made in a platinum vessel with a relatively large amount of fluoride and comparatively little amorphous silicic acid or silicate (large amounts of quartz do not influence the reaction); the test will be negative, on the other hand, if made in platinum with no silicic acid, or, strange to say, when only quartz is present with the fluoride. The reason for this different behavior lies in the difficulty with which quartz is attacked by hydrofluoric acid.

Daniel recommends the following method for performing the test:

Mix the substance to be tested for fluorine with about three times as much (by volume) of ignited quartz powder, place the mixture in a test tube, and stir it into a thin paste with concentrated sulfuric acid. Close the test tube with a cork in which one hole has been bored and an opening cut in the side. Through the hole in the cork insert a glass rod blackened with asphalt paint, and on the bottom of the rod suspend a drop of water; push this rod down into the tube until it is only a distance equal to about $1\frac{1}{2}$ times the diameter of the test tube from the paste in the bottom. Gently heat the tube and its contents over a small flame, and if a fluoride is present a white film of H_4SiO_4 will be formed in the drop of water and will be shown plainly in contrast to the black rod. In a tube with 1-cm diameter, fluorine equivalent to 1 mg CaF_2 may be detected; with a tube of only 0.5-cm diameter, as little as 0.1 mg CaF_2 will give the test. When using a tube of small diameter, it is best to add the sulfuric acid through a small capillary pipet to avoid wetting the sides of the tube.

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* *Z. anorg. Chem.*, **38**, 299 (1904).

If the substance contains considerable amorphous silica, or when an oxyfluoride, such as topaz, is present, which is hard to decompose with sulfuric acid, the test will fail, and it is then necessary to make use of the etching test.

3. **The Etching Test.** — Place the substance to be tested for fluoride in a platinum crucible, add some concentrated sulfuric acid, and cover the crucible with a watch glass whose convex side has a thin coating of beeswax through which a few letters have been scratched with a pointed match. On warming the contents of the crucible, the glass will be etched at the places where the escaping gas comes in contact with it, if a fluoride was originally present. By placing a little ice on the upper concave side of the watch glass, the wax coating will not melt during the experiment.

If it is desired to detect the presence of a trace of fluorine, allow the crucible to stand covered with the watch glass for twelve hours and then heat for a few minutes. The presence of only 0.3 mg CaF_2 is sufficient to give this test, provided a small crucible is used.

If the fluoride contained silica (as in topaz, tourmaline, and other minerals), the etching test will be negative, for even if the fluorine escapes, it will be in the form of silicon fluoride, which does not attack glass.

To detect small amounts of fluoride in silicates, it is necessary first to transform the fluorine into calcium fluoride and to subject the latter compound to the test.

To obtain the fluorine as calcium fluoride, proceed as follows:

Fuse the finely pulverized silicate with six to eight times as much sodium carbonate in a platinum crucible, and treat the melt with water after it is cold. A solution is thus obtained in which all the fluorine is present as sodium fluoride, together with sodium silicate. Precipitate the silicic acid by adding considerable ammonium carbonate to the solution, warming it slightly, and allowing it to stand twelve hours. After filtering off the silica, evaporate the solution to a small volume, and add a little phenolphthalein, which will impart a pink color to the solution on account of its being slightly alkaline. Carefully add hydrochloric acid until the stirred solution becomes colorless, and heat to boiling, when the color will reappear. Again decolorize the solution with hydrochloric acid after it has become cold, and repeat the process until the solution becomes only faintly colored on boiling it.

Now add calcium chloride solution and again boil. The precipitate consists of calcium carbonate and calcium fluoride; filter it off, wash, dry, and ignite it in a platinum crucible. Treat the ash with dilute acetic acid, evaporate to dryness, triturate with water, and filter off the undissolved calcium fluoride. After drying the precipitate and burning the filter, it is ready for the etching test.

4. **Silver Nitrate** causes no precipitation from solutions of soluble fluorides.

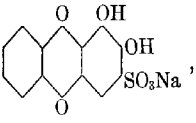
5. **Barium Acetate** precipitates barium fluoride soluble in an excess of mineral acid and in ammonium salts. Traces of fluorine present as preservative in foods, liquors, etc., may be detected by adding a little potassium sulfate (about 0.3 g) to the solution, heating it to boiling, and slowly introducing 10 ml of 10 per cent barium acetate solution. The precipitate of barium sulfate and fluoride is then subjected to the etching test.*

* Cf. Blarez, *Chem. News*, **91**, 39; also Woodman and Talbot, *J. Am. Chem. Soc.*, **27**, 1437.

6. **Calcium Chloride** gives a white, slimy precipitate, difficultly soluble in hydrochloric and nitric acids, but almost insoluble in acetic acid. On account of its slimy consistency, the precipitated calcium fluoride is extremely hard to filter; but by precipitating it in the presence of calcium carbonate a mixture is obtained which can be readily filtered. After igniting and treating with acetic acid, the precipitate is changed to soluble calcium acetate and insoluble calcium fluoride; it is now much denser and can be filtered readily.

7. **Ferric Chloride** produces in concentrated solutions of alkali fluorides a white, crystalline precipitate corresponding to the general formula $M_3[FeF_6]$. These salts, which are analogous to cryolite, $Na_3[AlF_6]$, are difficultly soluble in water, and their saturated, aqueous solutions do not give the iron reaction upon the addition of potassium thiocyanate, except after the addition of acid. These complex fluorides also are slightly decomposed by ammonia, forming a basic ferric fluoride.

8. **Lanthanum Acetate,** $La(C_2H_3O_2)_3$, produces a gelatinous precipitate which slowly changes to crystalline $LaF_3 \cdot 3\,H_2O$. The precipitate is difficultly soluble in dilute acids but is gradually dissolved by strong mineral acids.

9. **Zirconium Chloride,** $ZrCl_4$, and **Sodium Alizarin Sulfonate,** $C_{14}H_7O_4SO_3Na$ or  , react to give a dark reddish violet compound, but the addition of fluoride ions causes decolorization, due to the formation of colorless $[ZrF_6]^{--}$ complex anions. Large quantities of sulfate, thiosulfate, phosphate, arsenate, and oxalate interfere with the test.

Prepare test paper as follows: Heat zirconium oxide with 2 *N* hydrochloric acid and filter; the solution should contain about 0.5 mg Zr per ml. Treat a little of the zirconium chloride solution with a slight excess of sodium alizarin sulfonate in alcohol. To determine whether an excess is present, shake a little of the solution with ether; the ether will assume a yellow color if an excess of alizarin has been added. Heat the mixture for 10 minutes in boiling water; impregnate filter paper with the solution, and dry.

To test for fluoride, add 1 drop of 50 per cent acetic acid to a piece of the test paper, and upon the moist, red spot place a drop of the neutral solution to be tested. If fluoride anions are present, the spot will turn yellow. As little as 1 γ of F^- can be detected, but with small quantities of fluoride it is best to heat the paper in steam.

If oxalate is present, first decompose it by heating the sample before making the test. If sulfate is present, add some benzidine hydrochloride to the test solution, and place a drop of the solution containing the benzidine sulfate precipitate in suspension on the test paper; the red zirconium-alizarin spot can then be seen on the back of the paper.

METHODS FOR GETTING INSOLUBLE FLUORIDES INTO SOLUTION

(*a*) Calcium fluoride alone cannot be decomposed completely by fusing with sodium carbonate. The aqueous solution of the melt always contains a considerable amount of sodium fluoride, but never the total amount of the fluorine. If however, the fluoride is mixed with silica or a silicate, complete decomposition can be effected by fusing with sodium carbonate. The silica decomposes calcium fluoride, forming calcium fluosilicate and calcium silicate, salts which are decomposed by fusion with sodium carbonate.

On treating the melt with water, sodium fluoride and sodium silicate go into solution, while the calcium is left behind on the carbonate and can be dissolved by treatment with dilute hydrochloric acid. To detect fluorine in silicates, they should first be subjected to sodium carbonate fusion.

(*b*) All fluorides are decomposed by heating with concentrated sulfuric acid, being changed to sulfates.

Reactions in the Dry Way

Most fluorides are unchanged by ignition. By heating them with silica in moist air, they are all more or less completely decomposed:

$$CaF_2 + H_2O + SiO_2 \rightarrow CaSiO_3 + H_2F_2 \uparrow$$

$$2\,H_2F_2 + SiO_2 \rightarrow SiF_4 \uparrow + 2\,H_2O$$

The acid fluorides gives off hydrofluoric acid on ignition, whereby the glass tube in which they are heated becomes etched.

FLUOSILICIC ACID, H_2SiF_6

Preparation. — As we have seen, this acid is formed by the action of silicon fluoride upon water:

$$3\ SiF_4 + 4\ H_2O \rightarrow 2\ H_2[SiF_6] + H_4SiO_4$$

If the silicic acid is filtered off, a strongly acid solution is obtained containing fluosilicic acid. By evaporating the solution, the acid is decomposed into silicon fluoride and hydrofluoric acid,

$$H_2[SiF_6] \rightarrow SiF_4\uparrow + H_2F_2\uparrow$$

so that fluosilicic acid itself is known only in aqueous solution, although its salts are very stable.

Solubility. — Most fluosilicates are soluble in water; the potassium and barium salts form exceptions, being difficultly soluble in water and insoluble in alcohol.

Reactions in the Wet Way

A solution of sodium fluosilicate should be used.

1. **Dilute Sulfuric Acid** causes only very slight decomposition.

2. **Concentrated Sulfuric Acid** decomposes fluosilicates, evolving silicon fluoride and hydrofluoric acid:

$$Na_2SiF_6 + H_2SO_4 \rightarrow Na_2SO_4 + SiF_4\uparrow + H_2F_2\uparrow$$

If the reaction is performed in a platinum crucible, the escaping gas will etch glass, and will cause a drop of water to become turbid.

3. **Ammonia** decomposes all soluble fluosilicates, with separation of silicic acid:

$$Na_2SiF_6 + 4\ NH_4OH \rightarrow 2\ NaF + 4\ NH_4F + H_4SiO_4$$

4. **Barium Chloride** gives a crystalline precipitate (1 g $Ba[SiF_6]$ dissolves in about 3750 ml of water at 17°).

5. **Potassium Chloride** produces, from solutions which are not too dilute, a gelatinous precipitate of potassium fluosilicate, which is difficultly soluble in water (1 g of $K_2[SiF_6]$ dissolves in 835 ml of water at 17°) and much more insoluble in an excess of potassium chloride or in alcohol, but soluble in ammonium chloride.

6. **Silver Nitrate** produces no precipitation.

7. **Potassium and Sodium Hydroxides** react in the same way as ammonia, but the silicic acid remains in solution as alkali silicate.

Reactions in the Dry Way

Fluosilicates are decomposed on being heated into fluoride of the metal and silicon fluoride:

$$K_2SiF_6 \rightarrow 2\ KF + SiF_4\uparrow$$

The escaping gas renders a drop of water turbid, and the residue gives all the reactions of a fluoride.

GROUP VII

NON-VOLATILE ACIDS WHICH FORM SOLUBLE SALTS WITH THE ALKALIES

SILICIC ACID, H_4SiO_4 AND H_2SiO_3

Occurrence. — The above acids, from which very stable salts are derived, are not known in the free state; the same is true of carbonic and sulfurous acids. There are, however, amorphous, natural minerals consisting of hydrated silica with varying amounts of water: water opal with about 36 per cent water, ordinary opal with 3 to 13 per cent water, and hyalite with about 3 per cent water; but none of these substances represents a compound of constant composition.

The anhydride SiO_2 occurs in rhombohedral crystals as quartz, whose prismatic faces are almost always striated horizontally; and as tridymite, also crystallizing in the hexagonal system. The amorphous silicic acid is often found mixed with the crystallized anhydride as flint, agate, chalcedony, jasper, etc. Silicic acid is, however, most frequently found in the form of its salts, the silicates.

Preparation and Properties. — Silicic acid can be very readily obtained by the hydrolysis of its fluoride,

$$3\,SiF_4 + 4\,H_2O \rightarrow 2\,H_2SiF_6 + H_4SiO_4$$

or by the decomposition of alkali silicates (water-glass) with acids:

$$Na_2SiO_3 + 2\,HCl \rightarrow 2\,NaCl + H_2SiO_3$$

The silicic acid thus obtained forms an amorphous, gelatinous mass, appreciably soluble in water and acids, and readily soluble in even dilute solutions of caustic alkalies or alkaline carbonates. Thus freshly precipitated silicic acid will be readily and completely dissolved by a short digestion with 5 per cent (or even 1 per cent) sodium carbonate solution on the water-bath. On being dried, silicic acid gradually loses water, and at a gentle red heat is changed into the anhydride. According to the extent to which the dehydration has gone, the solubility of the silicic acid diminishes both in acids and in alkalies.

1. Air-dried silicic acid, with 16.65 per cent of water, corresponding to the formula $3\,SiO_2 \cdot 2\,H_2O$, is perceptibly soluble in acids, and completely dissolved by digestion for one-quarter to one-half an hour with 1 per cent sodium carbonate solution on the water-bath.

2. *Silicic acid dried at* 100° with 13.60 per cent of water, corresponding to the formula $2\,SiO_2 \cdot H_2O$, is *practically insoluble in acids*, but can be dissolved by digesting for one-quarter hour with 1 per cent sodium carbonate solution upon the water-bath, or more readily by boiling.

3. Silicic acid dried at 200°, with 5.66 per cent of water, corresponding to the formula $5\,SiO_2 \cdot H_2O$, and the acid dried at 300°, with 3.40 per cent of water, corresponding to the formula $9\,SiO_2 \cdot H_2O$, dissolve slowly by digestion with 1 per cent sodium carbonate solution on the water-bath.

4. The anhydride obtained by gentle ignition to a dull-red heat is only partly dissolved by 1 per cent or by 5 per cent sodium carbonate after half an hour's diges-

tion on the water-bath; but is dissolved after boiling for two hours with the sodium carbonate solution.

5. The strongly ignited anhydride is dissolved slowly by 5 per cent sodium carbonate solution after repeated boiling for a long time, but is readily dissolved by boiling with concentrated caustic soda or potash.

6. The native anhydride, quartz, after being powdered in an agate mortar, is practically insoluble in 5 per cent sodium carbonate solution, and very difficultly soluble in boiling caustic alkali. If it is in the form of an extremely fine powder, it can be dissolved by boiling with 5 per cent sodium carbonate solution (Lunge and Millberg).

It follows from the above that the solubility of silicic acid (and of its anhydride) in alkali carbonates depends largely upon the fineness of the material.

Silicic acid, as well as its anhydride, is soluble in aqueous hydrofluoric acid, forming fluosilicic acid:

$$SiO_2 + 6\,HF \rightarrow 2\,H_2O + H_2SiF_6$$

By evaporating this solution hydrofluoric acid and silicon fluoride are evolved, and small amounts of silicic acid are left behind. In order, then, to volatilize silicic acid completely by means of hydrofluoric acid, the hydrolytic action of water must be prevented, which is effected by the addition of a little concentrated sulfuric acid. The procedure is as follows:

Moisten the substance in a platinum crucible with a very little water, add not more than ½ ml of concentrated sulfuric acid and then the hydrofluoric acid. Evaporate the mixture on the water-bath, or suspend the crucible in a large crucible, and heat the latter until the hydrofluoric acid is expelled, cool, add another portion of hydrofluoric acid, and again evaporate. If a very large quantity of silicic acid is present it may be necessary to treat with hydrofluoric acid a third time. It is better to proceed in this way than to add a large quantity of hydrofluoric acid at one time. Finally drive off the sulfuric acid by heating directly over a small flame.

The salts of silicic acid, the silicates, are exceedingly numerous, and are usually very stable. Many of them are so stable that they are not attacked by concentrated mineral acids other than hydrofluoric acid, while others are easily decomposed.

The different silicates are classified according to their solubility into

A. Water-soluble silicates.

B. Water-insoluble silicates, which are again subdivided into

(*a*) Silicates decomposable by acids,

(*b*) Silicates undecomposable by acids.

Silicic acid is not soluble in water except to form colloidal solutions, and it yields scarcely any hydrogen ions. In this respect it is a very weak acid, but, since it is practically non-volatile, it is capable of expelling the acid from the salts of strong acids provided the base itself is not volatile at the temperature at which the salt is decomposed. The silicates, therefore, are very stable compounds particularly toward heat. The natural silicates are derived from orthosilicic acid, H_4SiO_4, from metasilicic acid, H_2SiO_3, and also from polysilicic acids such as $H_4Si_3O_8$, and $H_{12}Si_5O_{12}$. The solubility of the silicate depends upon two factors — the solubility of the oxide of the base and the proportion of silicic acid present. As a general rule, the salts of ortho- and metasilicic acids are more soluble than those of the polysilicic acids. Thus sodium and potassium ortho- and metasilicates are soluble in water, whereas a polysilicate may contain alkali as its principal base and yet be undecomposable by

concentrated hydrochloric acid. Such silicates may, however, be decomposed by melting with a solid acid such as boric acid, or by treating with mineral acid in a sealed tube.

Salts of bases of which the ignited oxides are very insoluble, such as Al_2O_3, sometimes form insoluble silicates of the ortho- and meta- types.

A. Water-soluble Silicates

The silicates which are soluble in water, or "water-glasses," are obtained by fusing silica or a silicate with caustic alkali or alkali carbonate:

$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2\uparrow$$

1. **Behavior Toward Acids.** — The aqueous solution of an alkali silicate reacts strongly alkaline, showing that the salt is hydrolyzed to a marked degree:

$$SiO_3^{--} + 2\,H_2O \rightarrow 2\,OH^- + H_2SiO_3$$

The silicic acid set free by the hydrolysis is present as hydrosol in the solution. By the addition of acid the alkali hydroxide is converted into salt and a part of the silicic acid is coagulated, provided the solution is not too dilute. The precipitation is by no means quantitative; a considerable quantity of silicic acid remains in solution and, in fact, under some conditions all of it may remain dissolved in the dilute acid. If, namely, a 10 per cent water-glass solution is poured quickly into hydrochloric acid of density 1.1 to 1.3, there is no precipitation. After standing some time, however, the entire contents of the beaker are changed to a jelly. From 1 per cent solutions treated similarly with acid, no precipitate appears even after standing a year.

The silicic acid which is precipitated upon the addition of acid is, therefore, appreciably soluble in dilute acids. In order to separate silicic acid completely from a solution of water-glass, the hydrated acid must be changed into the less hydrated acid, $2\,SiO_2 \cdot H_2O$, by heating at 100° C (cf. p. 443). For this purpose acidify the water-glass solution with hydrochloric acid (or nitric or sulfuric acid) and evaporate on the water-bath to complete dryness (the mass must no longer smell of acid). Moisten the dry residue with strong acid, warm slightly, dilute, and filter off the silicic acid. The small amount of silica remaining in solution can be removed almost entirely by a second evaporation of the filtrate.

2. **Behavior Toward Ammonium Salts.** — If a solution of water-glass is treated with an ammonium salt, the silicic acid will, for the most part, be precipitated as hydroxide; the precipitation is not quantitative, but more complete than is obtained by the addition of cold, dilute acid:

$$SiO_3^{--} + 2\,NH_4^+ \rightarrow 2\,NH_3 + H_2SiO_3$$

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

The hydroxide ions have a marked solvent action upon the silicic acid. For this reason the precipitation is more complete with an ammonium salt of a strong acid than with that of a weak acid, which is already hydrolyzed to a considerable extent. Boiling off the ammonia helps to make the reaction complete. The use of ammonium carbonate, though less satisfactory than ammonium chloride, is necessary when it is desired to test the solution for chloride.

Silicic acid is more completely precipitated by hexamminezinc hydroxide than by ammonium carbonate,

$$SiO_3^{--} + [Zn(NH_3)_4](OH)_2 \rightarrow 2\,OH^- + 6\,NH_3\uparrow + ZnSiO_3$$

because the zinc silicate formed by the reaction is much more difficultly soluble in dilute alkaline solution than is the free silicic acid.

The separation of silicic acid from a solution of water-glass by means of ammonium carbonate may be illustrated by a common example. Many rocks (particularly the zircon-syenite of Norway and Greenland, many granites and basalts) contain small amounts of sodalite, $NaCl \cdot 3\,NaAlSiO_4$, a chloride-silicate of the leucite group. In order to detect the chlorine in such a rock, the following process may be used: Fuse the finely powdered silicate with six times as much sodium carbonate in a platinum crucible, extract the product of the fusion with cold water, and filter. The filtrate contains all the chlorine as sodium chloride in the presence of sodium silicate. Treat the solution with ammonium carbonate, warm gently, allow to stand twelve hours, and then filter off the precipitated silicic acid. In order to separate the rest of the silicic acid, add a little hexamminezinc hydroxide and boil the solution until it no longer smells of ammonia. Filter off the precipitated zinc silicate and zinc oxide, acidify the filtrate with nitric acid, and test for chloride with silver nitrate.

To prepare the hexamminezinc hydroxide dissolve pure zinc in nitric acid, treat the solution with potassium hydroxide solution until it is neutral, and dissolve the filtered and washed zinc hydroxide in 6-normal ammonium hydroxide.

3. **Ammonium Molybdate and Benzidine.** — Silicic acid, like phosphoric and arsenic acids, forms a complex acid with molybdic acid, but, unlike these other acids, the ammonium salt, $(NH_4)_4SiO_4 \cdot 12\,MoO_3$, is soluble in nitric acid. The following test serves to detect as little as 0.1 γ of dissolved SiO_2 and can be used after a precipitate of ammonium phosphomolybdate has been removed by filtration.

As reagents use (1) ammonium molybdate solution prepared by dissolving 5 g of the commercial salt in 100 ml of water and pouring into 35 ml of 6 *N* HNO_3; (2) benzidine solution prepared by dissolving 0.5 g of benzidine or benzidine hydrochloride in 10 ml of glacial acetic acid and diluting with water to 100 ml; (3) saturated sodium acetate solution.

Place 1 drop of the solution to be tested (not over 0.5 *N* in acid) in a small porcelain crucible, and add 1 drop of ammonium molybdate solution. Heat gently over wire gauze until bubbles escape. Cool, and to the cold solution add 1 drop of benzidine solution and a few drops of sodium acetate solution. A blue color shows the presence of SiO_2 (Feigl).

The crucible must be treated with the reagents before applying the test, in order to make sure that SiO_2 is not obtained from it. The blue color has been called " molybdenum blue " but although it is caused by reduction of the Mo in the complex acid it is probably true that a blue quinoidal compound is formed at the same time by the oxidation of the benzidine.

B. Silicates Insoluble in Water

(a) Decomposable by Acids

A large number of native silicates are decomposed by evaporation with hydrochloric acid, the silica being deposited sometimes in the form of a jelly and sometimes in the form of a powdery mass. All zeolites, and a number of artificial silicates (such as Portland and Roman cements) belong to this class of silicates.

To remove all the silicic acid from these silicates, treat the finely powdered mineral with dilute hydrochloric acid and evaporate to dryness on the water-bath. During the evaporation to dryness salts like aluminum chloride (ferric chloride, etc.) are subject to hydrolysis and are converted to some extent into oxide or basic salt, insoluble in water. Therefore, in order to separate the silicic acid from the salts, it is first necessary to convert such oxides of basic salts back into chlorides. This is accomplished by moistening the dry residue with concentrated hydrochloric acid. After warming the acid with the residue for about ten minutes, dilute with hot water, boil, and filter off the silicic acid, using an ashless filter.

The purity of the residual silicic acid must always be tested. For this purpose, place the well-washed precipitate, together with the filter paper, in a weighed platinum crucible which rests in an inclined position on a triangle. Dry carefully by a low flame placed in front of the crucible, and then ignite at as low a temperature as possible, with the flame now at the base of the crucible, until the carbon of the filter is all consumed. Then, for the first time, ignite strongly, cool somewhat, place in a desiccator, and weigh when perfectly cool. Treat with hydrofluoric and sulfuric acids as described on page 444, ignite, and weigh after proper cooling. A difference in the weights before and after the treatment with these acids shows not only the presence of silica, but also the quantity of it. This quantitative method is necessary for the detection of small quantities of silicic acid. If the silicic acid were pure, nothing should remain after the evaporation of the sulfuric acid. Almost always a small residue of aluminum and ferric oxides remains, which in most cases can be neglected. If considerable residue is left, it should always be tested for titanic acid, barium sulfate, and possibly tin dioxide.

To identify the silicic acid qualitatively, Daniel's tetrafluoride test is satisfactory.*

DANIEL'S TETRAFLUORIDE TEST

Ignite the well-washed precipitate, as described above, in a platinum crucible, then triturate in a mortar with three times as much potassium sodium carbonate, and fuse the mixture in the crucible. After cooling the melt, soften it by heating with a little water and treat with dilute sulfuric acid to decompose the excess of carbonate as well as the salt of silicic acid formed during the fusion. Heat the mixture in the crucible, by placing the crucible upon a piece of absestos board, and evaporate nearly to dryness, or until a thick jelly of silicic acid remains. After cooling, add three times as much fluorspar as there was original precipitate, a little magnesite, and enough concentrated sulfuric acid to make a thin paste. After mixing the contents of the crucible with the aid of a stout platinum wire, place a drop of water on the inside of the crucible cover, which is partly painted with asphaltum, place the cover on the crucible, and heat the contents gently. From time to time, raise the cover to see whether the water has become turbid. It frequently happens that the water becomes turbid, and then, provided a large excess of hydrofluoric acid is present, the turbidity disappears. For this reason the cover must be inspected frequently in order not to miss any temporary turbidity.

The tetrafluoride test for silicic acid is very sensitive if the reaction is carried out in a very small platinum crucible. If such a crucible is not at hand, with a capacity of, say, 0.5 to 1 ml, it is better to test by the quantitative method if less than 0.01 g of silicic acid is present.

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* *Z. anorg. Chem.*, **38**, 299 (1904).

(b) *Undecomposable by Acids*

Most silicates, the feldspars, micas, artificial glasses, porcelain, etc., belong to this class. In order to remove the silicic acid from such substances, they must be

1. Fused with an alkali carbonate,
2. Fused with lead oxide or boron trioxide, or
3. Heated with sulfuric and hydrofluoric acids.

The effect of fusing a silicate with an alkali carbonate, or with a fusible oxide of some metal such as lead, is to increase the proportion of base in the silicate molecule. When the proportion of base is increased, the solubility of the silicate is also increased provided the base is itself readily soluble in acid. It is not at all necessary, therefore, to get all the silicic acid in the form of sodium silicate or of lead silicate, by fusing with sodium carbonate or with lead oxide, but it is sufficient if the silicate is coverted into a silicate which is decomposable by acid. For this reason the fusion with sodium carbonate or with lead oxide is often said to *open up* the silicate. It converts the silicate into the ortho- or meta- type and makes the silicate decomposable by acid. Thus after fusing with sodium carbonate, for example, it will be found that part of the sodium is converted into water-soluble sodium silicate and part of it into a double silicate which is decomposable by acid. A part of the sodium and a part of the silicate can be dissolved out of the fused mass by treatment with hot water.

1. *Fusion with an Alkali Carbonate.* — This method is commonly used when it is desired to detect the presence of silicic acid and of all the bases except the alkalies.

Mix the finely powdered substance with 4–6 times as much calcined sodium carbonate (or a mixture of equal parts of sodium and potassium carbonates, which melts lower than sodium carbonate alone), and fuse the mixture in a platinum crucible, heating carefully at first to avoid spattering from too violent evolution of carbon dioxide. Gradually increase the temperature until the full heat of the burner is reached, and continue fusing until the molten mass is quiet, and then heat for about a quarter of an hour over the blast lamp. Make a spiral by winding some platinum wire around a stirring rod, and insert the spiral in the melt. Cool the crucible quickly by directing a blast of cold air against its sides, and while the contents of the crucible are still warm, but not hot enough to spatter badly, cover with a little water from the wash bottle. After a few minutes the fusion can usually be withdrawn with the aid of the platinum spiral. Treat the product of the fusion as described on page 447.

2. *Fusion with Lead Oxide or Boron Trioxide.* — These methods are very rarely used in qualitative analysis, so that it will not be necessary to describe them here. They play a more important part in quantitative analysis and will be described, therefore, in the second volume of this book.

3. *Decomposition by Hydrofluoric Acid.* — This method is used principally when a silicate is to be examined for alkalies, titanic acid, or barium.

Treat the finely powdered silicate in a platinum dish with about 2 ml of pure sulfuric acid (1 vol. concentrated acid and 2 vols. of water) and about 5 ml of pure 48 per cent hydrofluoric acid. Evaporate the mixture on the water-bath, stirring the mass from time to time with a thick platinum wire until it no longer smells of hydrofluoric acid. Add 5 ml more of hydrofluoric acid and again evaporate, finally heating the dish very carefully over the free flame, under a good hood, until the greater part of the sulfuric acid is expelled. The mass should not be ignited strongly, for a part of the sulfate may then be changed to an oxide insoluble in water. The sulfates of iron and aluminum, for example, are decomposed on ignition. After cooling,

treat the mass with water, and usually everything will gradually go into solution. If a residue remains, test it for barium sulfate, titanic acid, and tinstone. The solution can be used for the alkali tests, or for the tests for the other metals, if it is desired.

Reactions in the Dry Way

If silicic acid or a silicate is heated in the salt of phosphorus bead, the metallic oxide will dissolve, while the silicic acid itself will be left as a white gelatinous mass, suspended in the bead (skeleton bead). This reaction, however, is not infallible, for certain silicates of the zeolite group dissolve in the bead without the formation of the skeleton.

SILICON, Si. At. Wt. 28.3, At. No. 14

Properties. — Silicon exists in two modifications, one of which is crystalline, while the other is amorphous. Amorphous silicon is a dark brown powder, which can be oxidized by heating in the air. The crystalline modification remains unchanged on ignition in pure air or in oxygen, but if the air contains carbon dioxide, it is oxidized to silicon dioxide with deposition of carbon:

$$CO_2 + Si \rightarrow SiO_2 + C$$

Crystallized silicon is not attacked by any acid, but is readily dissolved by boiling with concentrated caustic alkali with evolution of hydrogen:

$$Si + 2\,OH^- + H_2O \rightarrow SiO_3^{--} + 2\,H_2\uparrow$$

Silicon unites with many metals, forming silicides. The silicides of the light metals, magnesium, calcium, etc., are decomposed by dilute hydrochloric acid with the formation of spontaneously combustible silicon hydride:

$$Mg_2Si + 4\,H^+ \rightarrow 2\,Mg^{++} + H_4Si\uparrow$$

The hydride of silicon is not spontaneously combustible when pure, only when it is contaminated with hydrogen, as it invariably is.

In order to detect the presence of silicon in such a compound, treat it with nitric acid, which oxidizes the greater part of the silicon to silicic acid.

DETECTION OF SILICON IN IRON AND STEEL

If it is a question of detecting the presence of silicon in the different kinds of ferrous alloys (steel, cast iron, etc.), take a large quantity of material, for the amount of iron silicide present is usually very small. Place 5 to 10 g of the material (best in the form of borings) in a large beaker and treat with 60 ml of 6-normal nitric acid. A violent reaction at once takes place with evolution of brown nitrous fumes. As soon as this action lessens, heat the solution to boiling, and continue heating until no more brown fumes are given off. Pour the solution into a 200-ml casserole and evaporate as far as possible upon the water-bath. Heat the residue carefully over a free flame until it is perfectly dry, and then ignite the mass until the nitrate is completely changed to oxide, when no more brown fumes will be evolved. After cooling, dissolve the mass in about 50 ml of concentrated hydrochloric acid, heat with constant stirring almost to boiling, evaporate nearly to dryness, take up in water, filter, and test the residue for silicic acid, by seeing whether it is volatile with sulfuric and hydrofluoric acids.

In the analysis of cast iron, the silicic acid obtained is contaminated with graphite, which can be removed by long ignition in a platinum crucible before treating with hydrofluoric and sulfuric acids.

DETECTION OF SILICON IN CARBORUNDUM AND METAL SILICIDES

Other silicides, such as carborundum, SiC, are not decomposed by nitric acid; they can be fused with caustic alkali in a silver crucible,

$$SiC + 4\,KOH + 2\,H_2O \rightarrow K_2SiO_3 + K_2CO_3 + 4\,H_2\uparrow$$

and on acidifying the melt, the silicic acid separates out. During the fusion the liberated hydrogen takes fire and forms water with the oxygen of the air.

Carborundum in the form of a fine powder is also easily decomposed by fusing with potassium carbonate. On removing the cover of the platinum crucible the blue flame of burning carbon monoxide is seen:

$$3\,K_2CO_3 + SiC \rightarrow K_2SiO_3 + 2\,K_2O + 4\,CO\uparrow$$

The method of fusing silicides with caustic alkali is often used for getting metallic silicides into solution. Many copper-silicon alloys are scarcely attacked by even aqua regia. If, however, they are fused with caustic alkali in a silver crucible, alkali silicate, metallic copper, and hydrogen are formed:

$$SiCu_2 + 2\,OH^- + H_2O \rightarrow SiO_3^{--} + 2\,Cu + 2\,H_2\uparrow$$

By treating the melt with water, the soluble potassium silicate can be separated from the copper.

PART IV. SYSTEMATIC ANALYSIS

The purpose of qualitative analysis is not simply to find out what elements are contained in a given substance, but the aim should also be to get a good idea of the relative amounts that are present. Manganese chloride, for example, is made from pyrolusite, and almost always contains traces of calcium, magnesium, nickel, cobalt, and iron. If the analyst should report that "the analyzed substance consists of chlorides of calcium, magnesium, nickel, cobalt, iron, and manganese," it is evident that one would get but a poor idea of the nature of the substance. The report should read: "The substance examined was manganese chloride, and contained traces of calcium, magnesium, etc., as impurities."

In order to be able to estimate the relative amounts of the different components of a substance, it is necessary to start with a known amount (usually $\frac{1}{2}$ to 1 g) and compare the size of the precipitates produced. It will be impossible for the beginner to estimate the amount of a precipitate obtained, if he has studied the reactions of the elements with unknown amounts of the different substances. If, however, he has learned to work with a known amount of material, he will soon be able to judge from the size of a precipitate the amount of element to which it corresponds.

It is a good plan first to work through the analysis of each group with a known solution containing 20 mg of each element and then it is comparatively easy to determine approximately how much of each element is present by the test obtained in the analysis of any unknown. Thus, starting with 1 g of the original substance, it is often convenient to designate a constituent as present in *small* quantity when apparently less than 10 mg is found, as present in *medium* quantity when from 10 to 50 mg is found, and as present in *large* quantity when distinctly more than 50 mg is present. Experience with large classes of students has shown that such judgments are correct in nearly nine cases out of ten. It should be borne in mind, moreover, that, for estimating small quantities of substances, qualitative tests are *more accurate* than any method of quantitative analysis. Thus all colorimetric methods of quantitative analysis are really based on qualitative tests. The comparison of a test with one obtained using a *known quantity* of substance often gives a more exact determination of the quantity present than a method in-

volving weighing or titration. This is because it is easy to prepare a solution containing, say, 1 mg per ml with an error of less than 5 parts per 1000, by dissolving 1000 times as much in a liter and thoroughly shaking; but it is more difficult to determine by direct weighing and with equal accuracy the presence of only 1 mg of substance. By the process of diluting and taking an aliquot part, it is possible to prepare a solution containing a very small known quantity of any soluble substance. For convenience, it is well to have solutions at hand containing exactly 10 mg per ml of each constituent. By taking three small drops of such a solution, approximately 1 mg of the constituent can be obtained.

Every analysis should be divided into three parts:

I. *The preliminary examination.*
II. *The examination for the metals (cations).*
III. *The examination for the negative elements (anions).*

The substance analyzed may be

A. *Solid* and *non-metallic.*
B. *A metal* or *an alloy.*
C. *A solution (liquid).*
D. *A gas.*

The whole amount of the substance at hand should never be used for the first analysis, but a portion should always be reserved for unforeseen accidents. The portion taken for analysis should be divided into two parts after the preliminary examination, the first part being used for the tests for the basic constituents and the other part for the tests for the acidic constituents.

At the start of an analysis, the substance should be carefully examined with the naked eye and with the microscope, and the results noted. Oftentimes the odor, color, and crystalline form give important clues as to the nature of the substance.

A. The Substance is Solid and Non-metallic*

I. PRELIMINARY EXAMINATION

This should never be omitted, for it often shows how the subsequent analysis may be considerably shortened, and sometimes makes the further examination unnecessary. It consists only of making the following few simple tests:

1. **Heating in the Closed Tube.** — By a closed tube is understood a small glass tube about 10 cm long and 0.5 cm in diameter sealed at

* See pages 488, 489 for B and C.

one end. Place a little of the substance in the tube so that none of it remains adhering to the sides, hold the tube in a nearly horizontal position, and cautiously heat in the flame, noting carefully whether any change takes place.

The Substance is Volatile

(*a*) *The substance sublimes completely* without any deposition of water; it contains no non-volatile substance.

The sublimate is white. The halogen compounds of ammonium,* mercuric and mercurous chloride and bromide, mercuric aminochloride, arsenic trioxide, and arsenic pentoxide may be present.

Arsenic peroxide melts before being changed into the trioxide.

The sublimate is colored —

Gray: all oxygen compounds of mercury, cyanide of mercury, free iodine, and arsenic.

Mercuric cyanide leaves a brown mass, paracyanide, which disappears only after long-continued heating.

Yellow: arsenic sulfide, sulfur, mercuric iodide.

Mercuric iodide becomes red immediately on being rubbed with a glass rod.

Grayish black: mercuric sulfide.

(*b*) *The substance is completely volatile, with separation of water* and gaseous products: most ammonium compounds (with the exception of those of the halogens) and free oxalic acid.

By very cautious heating, oxalic acid may be sublimed; it usually decomposes, however, into water, carbon monoxide, and carbon dioxide.

The Substance is only Partly Volatile

In this case gases and vapors may be evolved:

Oxygen from peroxide, nitrates, chlorates, iodates, etc.

Carbon dioxide from carbonates and organic substances; in the latter case it is usually accompanied with the separation of carbon and evolution of empyreumatic, combustible vapors.

Chlorine from chlorides of platinum, gold, copper, iron, etc.

Iodine from iodides, in the presence of oxidizing substances.

Sulfur from many sulfides and thiosulfates.

Arsenic from arsenites and arsenates, in the presence of carbon or organic substances.

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* In the case of ammonium salts, *e.g.*, NH_4Cl, this is not a true sublimation. When heated NH_4Cl gives NH_3 and HCl gases which combine again when chilled.

Arsenites are reduced without the aid of charcoal:

$$10\ K_3AsO_3 \rightarrow 6\ K_3AsO_4 + 6\ K_2O + As_4$$

Water from substances containing water of crystallization, from acid salts, organic substances, or from the phosphate, borate, chromate, vanadate, and tungstate of ammonium.

The water given off condenses in the cooler part of the tube and should be tested with litmus paper. If it reacts alkaline, it comes from ammonium compounds; if acid, it results from easily decomposable salts of the stronger acids.

Many fluorides when heated with water give off hydrofluoric acid, which etches the glass.

If a sublimate if formed, make the following experiment:

Mix a little of the substance with three times as much calcined sodium carbonate and heat in the closed tube. If *ammonium salts* are present, the smell of ammonia can be detected. *Mercury* compounds give a deposit of gray metal (cf. p. 108); *arsenic* and its oxygen compounds also usually yield the gray metal (but no globules), accompanied by a garlic odor.

The oxygen compounds of arsenic do not give the metal when heated with pure sodium carbonate. Commercial sodium carbonate, however, is usually contaminated with enough paper fibers to cause the reduction.

2. **Testing the Substance in the Bead.** — Make a borax or sodium phosphate bead in the loop of a very thin platinum wire (as described on p. 74), introduce it with a little of the substance into the oxidizing flame, observe the color of the bead both when it is hot and when it is cold, and then heat it in the reducing flame. Borax is generally used for this experiment, except when it is desired to test for silicic or titanic acids, or when the substance is white, in which case salt of phosphorus is used. Only colored oxides are capable of coloring the borax bead.

Some oxides are reduced to metal, so that the bead appears gray in the reducing flame (see following table). $CuSO_4$ is white when anhydrous, but becomes blue immediately on the addition of water.

The following substances impart a characteristic color to the bead: iron, manganese, nickel, cobalt, chromium, uranium, copper (didymium, cerium, vanadium, titanium, and tungsten).

Since the coloration varies with the temperature and with the amount of substance used, the results to be expected, with the necessary conditions, are summarized in the table on page 456. The following abbreviations are used: h = hot; c = cold; h-c = hot and cold; s.s. = slightly saturated; sat. = saturated.

3. **Heating a Little of the Substance upon Charcoal before the Blowpipe;** if deflagration takes place a nitrate, nitrite, chlorate, iodate, etc., may be present.

Color of the Bead	With Borax.		With Salt of Phosphorus.	
	In the Oxidizing Flame	In the Reducing Flame	In the Oxidizing Flame	In the Reducing Flame
Colorless	SiO_2 (without skeleton), alkaline earths, Hg, Pb, Bi, Sb, Cd, Zn, Sn, Ti	SiO_2 (without skeleton), alkaline earths and earths, Mn, Di, Ce, Cu (s.s.)	SiO_2 (usually with skeleton), alkaline earths and earths (sat. = turbid)	SiO_2 (usually with skeleton), alkaline earths and earths, Mn, Di, Ce, Cu (s.s.)
	W, Mo, Fe (s.s.—c)		W, Ti	
Gray		Ag, Pb, Bi, Sb, Cd, Zn, Ni		Ag, Pb, Bi, Sb, Cd, Zn, Ni
Yellow (or brown)	Fe (s.s.—h), Ag (h), Ce (h), U (h), V (h—sat.), Ni (c) (brown)	Ti (h), W (h), V (h), Mo (h)	Fe (s.s.—h), Ag (h), Fe (sat.—c), Ce (h), V (h), U (h), Ni (c) (brown)	Fe (h), Ti (h)
Green	Cr (c), Cu (h)	Fe (h—c), U, Cr, V (h)	Cr (c), Cu (h), Mo (h), U (c—sat.)	Cr (c), U (c), V (c), Mo (c)
Blue	Co (h—c), Cu (c)	Co (h—c)	Co (h—c), Cu (c)	Co (h—c), W (c)
Violet	Mn (h—c), Di (h—c), and Ni (with cobalt)		Mn (h—c), Di (h—c)	Ti (c)
Red	Fe (h—sat.) Ce (h)	Cu (sat.), opaque; when very slightly saturated and with a trace of Sn, ruby red and transparent.	Fe (h—sat.), Ce (h)	Cu as in the borax bead; Ti and W in the presence of iron = blood red

4. **Heating the Substance with Sodium Carbonate upon Charcoal before the Blowpipe.** — Mix as much of the substance as can be taken up on the end of a knife-blade with twice as much sodium carbonate (as described on p. 78), place it in a cavity on a piece of charcoal, and heat in the reducing flame of the blowpipe.

There is obtained:

(*a*) Metal without incrustation.	As malleable button: **Au, Ag, Sn, Cu,** which can be pressed flat in an agate mortar.
	As gray metallic particles: **Pt, Fe, Ni,** and **Co.** Pt may be pressed flat in an agate mortar; **Fe, Ni,** and Co are attracted by a magnet (cf. p. 76).
(*b*) Metal with incrustation...	As a brittle metallic button: Sb (white incrustation), **Bi** (yellow incrustation). The button may be reduced to a powder by grinding in an agate mortar.
	As a malleable button: **Pb** (yellow incrustation).
(*c*) Incrustation without metal.	White, yellow when hot: **Zn.**
	Brown: **Cd.**
	White: **As** (garlic-like odor).
(*d*) White, infusible, strongly luminous mass.....	**Ca, Sr, Mg, Al,** and rare earths.

(*e*) **Sulfur** compounds are reduced to sulfides. If the melt is placed on a bright silver coin and moistened with water, the silver is blackened (hepar reaction).

5. **Testing the Substance for Coloration of the Non-luminous Flame.** — Introduce a little of the substance on a platinum wire into the base of the flame (cf. p. 72), and then into the fusion zone. Afterwards moisten it with dilute hydrochloric acid and repeat the experiment. The following indications may be obtained:

Sodium gives a yellow monochromatic flame; a piece of sealing wax or a crystal of potassium dichromate appears yellow when illuminated by this flame.

Potassium (cesium and rubidium) gives a violet flame which is completely obliterated by the sodium flame. If the flame is observed through cobalt glass, the sodium flame disappears and the potassium flame appears pink.

Lithium gives a carmine-red flame (or a red line in the spectroscope).

Strontium also gives a carmine-red flame (which the spectroscope shows to consist of several lines in the orange, and a bright line in the blue).

Calcium gives a brick-red flame (in the spectroscope an orange and a green line are seen, both about an equal distance away from the sodium line).

Barium gives a greenish yellow flame.

With barium sulfate the green flame is either indistinct or not visible. In order to detect barium, heat a small portion of the substance in the upper reducing flame, cool, moisten with hydrochloric acid (odor of hydrogen sulfide) and again heat, when the barium flame can be easily seen.

Thallium gives an emerald-green flame.

If a green flame is obtained, test another portion of the substance for boric acid, by treating with concentrated sulfuric acid and bringing near the flame. A green color indicates the presence of boric acid, but if copper is present this test is not reliable.

By heating the solid substance with potassium ethyl sulfate in a test tube, boric acid is converted into $B(OC_2H_5)_3$, which is volatile and burns with a green flame. Copper chloride does not interfere with this test.

Lead, Arsenic, Antimony color the flame a faint blue, and **copper** compounds color the flame either green or blue.

Preliminary Examination for the Acidic Constituents (Anions)

1. **Dilute Sulfuric Acid** (2-normal). — Treat about a gram of the substance in a small test tube with dilute sulfuric acid, and note whether a reaction takes place in the cold (evolution of a gas).

The following gases can be recognized:

HCN from cyanides (odor).

Mercuric cyanide does not liberate HCN in this test.

H_2S from soluble sulfides (odor, and blackening of lead acetate paper).

NO_2 from nitrites (brown fumes).

SO_2 without separation of sulfur from sulfites (odor of burning sulfur).

SO_2 accompanied by separation of sulfur from thiosulfates; the deposited sulfur is yellow, particularly after warming.

CO_2 from carbonates or cyanates (barium hydroxide solution is rendered turbid).

By boiling with dilute sulfuric acid, soluble *ferro-* and *ferricyanides* are decomposed and evolve hydrocyanic acid; *acetates* set free acetic acid; *hypochlorites* evolve chlorine (which also takes place in the cold); while the *peroxides of the alkalies* and alkaline earths are decomposed with evolution of oxygen.

Alkali peroxides also evolve oxygen when treated with water. Cf. page 286.

2. **Concentrated Sulfuric Acid.** — If the substance does not react with dilute sulfuric acid, add 3 or 4 ml of concentrated sulfuric acid and heat. If the substance reacted with dilute sulfuric acid, it will react violently with concentrated sulfuric acid and the gas will come off so quickly that it will carry small particles of the sulfuric acid with it, which makes the gas appear to have a penetrating odor and may lead to a mistaken conclusion, especially since it will also cause barium hydroxide solution to become turbid.

In such a case, add dilute sulfuric acid drop by drop to a new portion of the substance until no further action takes place, then add 5 ml of concentrated sulfuric acid and heat the mixture.

Gases and vapors may be evolved, which are

(*a*) *Colorless*

HCl from chlorides, fuming in the air, with penetrating odor. The fumes do not cause a turbidity with water.

AgCl and $HgCl_2$ evolve HCl very slowly; the same is true of Hg_2Cl_2, and in this case SO_2 is also set free. Cf. page 302.

SiF_4 from fluorides, fuming in the air, with a penetrating odor, and causing a turbidity on coming in contact with water.

SiF_4 is formed on account of the experiment being performed in glass. In platinum and in the absence of silica, H_2F_2 would be evolved, which does not render water turbid.

SO_2, without separation of *sulfur*. If there was no evolution of sulfur dioxide on treatment of the substance with dilute sulfuric acid, the sulfur dioxide which now escapes must come from the sulfuric acid itself; a metal, sulfur, a sulfide, carbon, or non-volatile organic matter, such as tartaric acid, citric acid, sugar, starch, etc., must be present. If non-volatile organic matter is present, carbonization will take place on warming.

SO_2 with separation of *sulfur* indicates the presence of a sulfocyanate, if there was no action with dilute sulfuric acid.

CO from oxalates and other organic substances, and cyanates. It is an odorless gas, which does not fume in the air and burns with a blue flame.

(*b*) *Colored*

Cl_2, a yellow gas with a suffocating odor, turns iodo-starch paper blue, and indicates the presence of both a chloride and an oxidizing substance.

ClO_2, a yellow gas, which is very similar to chlorine, but which explodes violently on being heated, indicates a chlorate. If the substance deflagrates on being heated on charcoal, only a small portion of the substance should be used for the test with concentrated sulfuric acid; but if no explosion takes place on warming, more of the substance should be added.

HBr from bromides has a penetrating odor, fumes in the air, and is always colored yellowish brown by the presence of small amounts of bromine. The sulfuric acid is at first colored brown in the case of a colorless bromide, but becomes colorless on being boiled.

CrO_2Cl_2, brown (similar to bromine), results from the presence of a chloride and chromic acid.

I_2, violet. In the case of a colorless iodide, the sulfuric acid is at first colored brown by small amounts of iodide, and gray solid iodine is deposited if considerable iodide is present, which volatilizes on warming, forming violet vapors. If considerable iodide is used for this test, the sulfuric acid is reduced to SO_2, or even H_2S (cf. p. 315).

Mn_2O_7, violet, is formed from permanganic acid, and is decomposed with scintillation, often exploding, on being warmed.

NO_2, brown, with a penetrating odor, comes from nitrates.

After the preceding tests have been made, the next step is

Dissolving the Substance

As solvents the following are used:

1. Water.
2. Hydrochloric acid.
3. Nitric acid.
4. Aqua regia.

In most cases the first three solvents suffice, aqua regia being seldom necessary, as will be seen from the table on pages 462–463:

Qualitative analysis is based largely upon the different solubilities of typical salts. The measurement of the solubility, or quantity dissolved by a given volume of solvent, has occupied the attention of a great many chemists, and books have been written on this subject alone. All such data, however, when brought together and compared show that numerical values for the weight of solid dissolved by 100 g of water are hard to determine accurately for those very substances with which the analytical chemist is concerned, namely, the less soluble ones.

There are several ways of determining the solubility of a substance. One method is to shake an excess of the solid at a constant temperature until no more of the substance dissolves. Another method is to obtain a supersaturated solution of the substance and allow it to stand until no more of the salt deposits. A third method consists in forming the substance by metathesis and finding how much of the constituents must be present in order to obtain precipitation.

Unfortunately, every method of measurement involves some unavoidable error and with very insoluble substances this error is sometimes even larger than the actual quantity of substance dissolved. For example, if one were to determine the solubility of silver cyanide by taking a weighed quantity and finding how much was left after shaking with water, or by finding how much salt was left after evaporating the water to dryness, the analytical error involved could amount easily to 0.0010 g and only about 0.0002 g of the salt really dissolves. When we remember that some of the solubility measurements were made many years ago, it is not strange that there should be disagreements of this nature.

The difficulties involved in the measurement of the solubilities of crystalline substances are bad enough but those for amorphous or gelatinous substances are much

worse. When shaken with water for some time, any finely divided substance tends to form a suspension which will pass through ordinary filter paper and gelatinous substances form colloidal solutions. It is almost impossible to draw the line closely between true solutions, colloidal solutions, and supensions. Errors in determining the solubility due to the formation of colloidal solutions and suspensions may be enormous.

Other difficulties are involved. In actual analytical work, the chemist rarely has time to wait for perfect equilibrium to take place. In dissolving a substance, he usually gets an undersaturated solution, and in making precipitations he usually gets a supersaturated solution. Moreover, many substances like nickel sulfide, aluminum hydroxide, and silicic acid appear to be much more insoluble after they have stood in the air a short time than when freshly precipitated and although nickel sulfide is harder to precipitate than zinc sulfide, the latter dissolves more readily in cold, dilute acid.

The Solubility Table on pages 462–463 will give an approximate idea of the solubility of common salts. The numerical values show the weight in grams that will dissolve in 100 ml of water. When two values are given, the upper value refers to cold water and the lower to hot water. Blanks in the table mean either that the salt has not been studied or that it cannot be formed. For further information concerning difficultly soluble salts, consult the Table of Solubility Products on pages 21–23. The table inserted here is intended to give the student some idea of relative solubilities, to guide him in the laboratory work, but for accurate information he should consult authorities such as the *International Critical Tables*. In some cases, salts are marked "i" (insoluble) while others are marked "a" (soluble in acid) without any good reason for making the distinction. Values for the solubilities of difficultly soluble salts are also given for some salts, where the data were available, while other salts are marked "a" or "i" when they are actually more soluble. No attention has been paid to double salts, and when salts crystallize with different quantities of water, the attempt has been made to refer to the most common salt, but there are some inconsistencies.

Substances Soluble in Water

Of Acid Group I (p. 297) the following are soluble:

1. **Chlorides.** — All except **AgCl**, Cu_2Cl_2, Hg_2Cl_2, $PtCl_2$, **AuCl**, **BiOCl**, **SbOCl**, Mg_2OCl_2. $PbCl_2$ and **TlCl** are difficultly soluble.

2. **Bromides.** — The same as the chlorides.

3. **Iodides.** — All except **AgI**, Hg_2I_2, HgI_2, Cu_2I_2, PdI_2, **TlI**; PbI_2 is very difficultly soluble.

4. **Cyanides.** — Only the cyanides of the alkalies, alkaline earths, and mercury.

5. **Ferrocyanides.** — Only those of the alkalies and alkaline earths.

6. **Ferricyanides.** — Same as the ferrocyanides.

7. **Cobalticyanides.** — Only those of the alkalies, alkaline earths, and the ferric, mercuric, and lead salts.

8. **Thiocyanates.** — Those of the alkalies, alkaline earths, iron, cupric copper, and mercuric mercury.

9. **Hypochlorites.** — All.

SOLUBILITY TABLE

		Sodium	Potassium	Ammonium	Magnesium	Calcium	Strontium	Barium	Aluminum	Chromium	Zinc	Manganese	Nickel
1	Acetate	119 170	253 >500	148 d.	36 >67	37 29.7	s.	76.4 74	s. d.-i.	s. d.-i.	30 44.6	s.	16.6 —
2	Arsenate	26.7	v.s.	s. d.	i. 0.15	0.005	0.28 d.	0.06	a.	—	i.	i.	a.
3	Arsenite	v.s.	v.s.	v.s. d.	s. v.s.	a.	sl.s.	—	—	—	—	i.	a.
4	Borate	1.3 200	s.	s.	i. v.sl.	sl.s.	77	—	—	—	s.	—	—
5	Bromide	121	53 102	60 146	91 120	125 312	85 222	157 204	v.s.	* 200	471 675	300	113 155
6	Carbonate	7.1 45.5	112 156	100 d.	0.01	0.0015 0.0019	0.0011 0.065	0.002 0.006	—	—	s.	0.006	0.009
7	Chlorate	79 230	7.1 57	v.s.	57 74	178 v.s.	175 v.s.	27.4 111	v.s.	—	209	—	0.9
8	Chloride	35.7 39.8	34.7 57	30 76	53 73	60 159	44 101	31 59	70 s.d.	* i.(233)	432 615	151 656	64 87
9	Chromate	50 v.s.	63 79	40.5 d.	212 v.s.	16 20	0.12 3	0.003 0.004	—	—	s.	s.	s.
10	Cyanide	s. v.s.	v.s.	v.s. d.	s.	s. d.	v.s.	80	—	—	—	—	i.
11	Ferricyanide	18.9 67	33 78	v.s.	s.	v.s.	v.s.	s.	—	—	—	—	—
12	Ferrocyanide	32 161	28 91	s.	33	87 120	50 100	0.017 0.9	sl.s.	—	s.	s.	s.
13	Fluoride	4	92 v.s.	v.s.	0.009 i.	0.0016 0.0017	0.012	0.17	s.	s.	s.	i. d.	0.02
14	Hydroxide	42 347	100 178	s.	0.0009 0.004	0.19 0.077	0.41 21.8	3.5 95	i.	i.	0.0004	s.	s.
15	Iodide	158.7 >257	128 208	154 250	100 165	182 426	165 383	200 269	s.d.	—	430 510	s.	124 188
16	Nitrate	73 180	32 247	118 871	200 v.s.	102 376	40 100	8.7 34.2	64 v.s.d.	s.	325	s.d.	240
17	Oxalate	3.7 6.33	33 —	2.5 11.8	0.07 0.08	0.0007 0.0014	0.005 5	0.007 0.022	i.-s.	s.	0.008	s.	s.
18	Oxide	d. v.s.	d. v.s.	—	0.0006 0.0008	0.12d. 0.07d.	d.	d.	i.	i.	0.00016	i.	i.
19	Phosphate	v.s.	s.	v.s.	0.021	0.002	i.-s.	i.-s.	i.	s.	s.	s.	s.
20	Silicate	s.	s.	d.-i.	i.	0.0095	i.	i.	i.	—	i.	i.	i.
21	Sulfate	s.	6.8 24.1	71 194	26 74	0.24	0.011 0.011	0.0002 0.0004	31 98	* i.-s.	86	52 70	29 83
22	Sulfide	s.	s. v.s.	v.s. d.	d.-i.	0.012d. 0.461d.	s.d.	d.	d.	d.	s.	s.	0.0003
23	Thiocyanate	v.s.	217	128 v.s.	s.	v.s.	v.s.	43 s.	—	—	s.	s.	s.
24	Tartrate	29 66	12 278	6 d.	0.8 1.44	0.003 0.008	0.11 0.76	0.03 0.06	s.	sl.s.	s.	v.sl.	s.

* Chromium salts often exist in two modifications; one is much more soluble than the other.

Abbreviations used: a., soluble in acids; d., decomposed by water; d.-i., decomposed and product is insoluble; i., insoluble in water; s., soluble in water; v.s., very soluble in water; sl.s., slightly soluble; v.sl., very slightly soluble;

SOLUBILITY TABLE

Cobalt	Ferrous	Ferric	Silver	Lead	Mercurous	Mercuric	Cupric	Bismuth	Cadmium	Stannous	Stannic	Antimonous	Gold	Platinum	
s.	s.	d.-i.	1.0 2.52	45.6 200	0.75	25 100	7.2 20	d.-i.	v.s.	d.	—	—	—	—	1
a.	a.	a.	0.0008	a.	i.	v.sl.	a.	—	—	—	i.	—	—	—	2
a.	a.	a.	0.0012	a.	—	—	a.	—	—	—	—	—	—	—	3
—	—	—	sl.s.	a.	—	—	s.	—	a.	—	—	—	—	—	4
65 68	109 170	s.	8.4×10^{-6}	0.46 4.75	i.	0.5 25	v.s.	d.	57 162	85 222	s.d.	d.	s.	0.4	5
a.	0.0067	—	sl.s.	0.0001	—	—	a.	i.	i.	—	—	—	—	—	6
558	—	—	10 50	v.s.	s.	25	207 v.s.	—	298 487	—	—	—	—	—	7
45 105	65 105	75 536	0.0001	0.67 3.34	0.002 0.001	3 6 61 3	71 108	d.	140 150	84 270	s. d.	600	68	v.s.	8
a.	—	—	0.0014	a.	v.sl.	sl.s.	i.	i.	a.	—	s.	—	—	—	9
i.	—	—	0.00002	sl.s.	—	9.3 53	i.	—	1.7	—	—	—	d.	i.	10
a.	i.	—	0.00007	sl.s.	—	—.	i.	—	a.	i.	—	—	—	—	11
a.	—	i.	i.	i.	—	—	i.	—	a.	i.	i.	—	—	—	12
s.	sl.s.	sl.s.	182 205	0.06	s.d.	d.	sl.s.	—	4.35	v.s.	d.	384 563	—	s.	13
a.	a.	a.	i.	0.016	i.	i.	i.	i.	2.6×10^{-4}	0.0002	d.	—	i.	i.	14
159 420	s.	—	3×10^{-7}	0.04 4.36	v.sl.	v.sl.	—	i.d.	80 127	1.32 3.55	d.	d.	s.	s.d.	15
134 v.s.	70 167	s.	122 952	38 126	d.	v.s.	v.s.	d.	109 326	d.	d.	—	—	—	16
s.	0.02 0.03	v.s.	0.0034	0.002	a.	s.	0.0025	a.	0.003 0.009	—	—	—	—	—	17
i.	i.	i.	0.0013 0.0053	0.002	i.	0.0052 0.040	i.	i.	a.	i.	i.	i.	i.	i.	18
a.	a.	s.	0.0006	s.	a.	a.	a.	a.	a.	i.	i.	i.	—	—	19
i.	i.	i.	—	i.	—	—	—	—	a.	—	—	—	—	—	20
36 83	16 50	sl.s. d.	0.57 1.41	0.003 0.005	0.06 0.09	d.	31 203	d.	75 60	18	v.s. d.	d.	s. d.	s.	21
0.0003	i.	i.	i.	i.	i.	i.	i.	i.	a.	i.	i.	i.	i.	i.	22
s.	s.	s.	0.00002	s.	i.	0.07	i.	—	a.	—	—	—	—	—	23
sl.s.	0.88	s.	0.2	i.	v.sl.	a.	v.sl.	i.	sl.s.	s.	—	—	—	—	24

s.d., soluble with some decomposition.

Numbers refer to grams of salt dissolved in 100 ml. When two values are given, the upper is for cold water and the lower is for hot water.

Of Group II (p. 297) the following are soluble:

10. **Nitrites.** — All. Silver nitrite is difficultly soluble.

11. **Acetates.** — Silver and mercurous acetates and certain basic acetates are difficultly soluble.

12. **Cyanates.** — Those of the alkalies, alkaline earths, and most of the remaining ones. Silver and lead cyanates are insoluble.

13. **Sulfides.** — Only those of the alkalies and alkaline earths. CaS is difficultly soluble.

14. **Hypophosphites.** — All.

Of Group III (p. 297) the following are soluble:

15. **Sulfites.** — Those of the alkalies, and the bisulfites of the alkaline earths.

16. **Carbonates.** — Those of the alkalies; the bicarbonates of Ca, Sr, Ba, Mg, Mn are fairly soluble in cold water.

17. **Oxalates.** — Those of the alkalies; the remainder are difficultly soluble or insoluble. Most oxalates, however, with the exception of Ba, Ca, and Sr oxalates, form soluble complex salts with alkali oxalates.

18. **Iodates.** — Only those of the alkalies.

19. **Borates.** — Those of the alkalies. The remaining borates are all difficultly soluble in water, but soluble in ammonium chloride as a rule.

20. **Molybdates.** — Only those of the alkalies.

21. **Selenites.** — Those of the alkalies are readily soluble; the remaining ones are difficultly soluble.

22. **Selenates.** — All except the barium and lead salts.

23. **Tellurites.** — Only those of the alkalies.

24. **Tellurates.** — Only those of the alkalies.

25. **Tartrates.** — The normal tartrates of the alkalies, and lithium and sodium bitartrates. The remaining tartrates are insoluble in water, but are usually soluble in an excess of alkali tartrate solution, forming complex salts.

26. **Citrates.** — Only those of the alkalies are readily soluble in water. The insoluble citrates usually dissolve in an excess of alkali citrate solution.

27. **Pyrophosphates.** — Only those of the alkalies.

28. **Metaphosphates.** — Only those of the alkalies.

Of Group IV (p. 297) the following are soluble:

29. **Phosphates.** — Only those of the alkalies.

30. **Arsenites.** — Only those of the alkalies.

31. **Arsenates.** — Only those of the alkalies.

32. **Thiosulfates.** — Almost all are soluble, though the silver and barium salts are difficultly soluble.

33. **Chromates.** — Those of the alkalies, Ca, Sr, Mg, Zn, Mn, Fe, and Cu are soluble, the others are difficultly soluble or insoluble.

34. **Vanadates.** — The orthovanadates are unstable; the pyro-, meta-, and polyvanadates are soluble in water, as a rule. The lead and mercurous salts are insoluble, also the vanadates of the iron group.

35. **Periodates.** — All more or less soluble in water, except silver periodate, which is insoluble.

Of Group V (p. 298), the following are soluble:

36. **Nitrates.** — All except a few basic salts.

37. **Chlorates.** — All.

38. **Perchlorates.** — All.

39. **Manganates** and **Permanganates.** — **All.**

Of Group VI (p. 298), the following are soluble:

40. **Sulfates.** — All except the Ca, Ba, Sr, and Pb salts, and a few basic sulfates.

41. **Fluorides.** — Those of the alkalies, silver, and mercury; the remaining fluorides are difficultly soluble or insoluble in water.

Of Group VII (p. 298), the following are soluble:

42. **Silicates.** — Only those of the alkalies.

43. **Tungstates.** — Only those of the alkalies.

Of the salts insoluble in water, all dissolve in acid (hydrochloric or nitric) except AgCl, AgBr, AgI, AgCN, AuCl, $PtCl_2$, $BaSO_4$, $SrSO_4$, $PbSO_4$, HgS, Prussian blue, CaF_2, SnS_2 (mosaic gold), SiO_2, many silicates, fused $PbCrO_4$, and the strongly ignited oxides: Al_2O_3, Cr_2O_3, TiO_2, SnO_2, Sb_2O_4.* TiO_2, SnO_2, and Sb_2O_4 can be dissolved by long-continued boiling with concentrated hydrochloric acid.

Of the salts insoluble in acids, the following dissolve in aqua regia: $PtCl_2$, AuCl, HgS, Sb_2O_4, SnS_2, and Prussian blue (after long treatment).

The following substances are not dissolved by aqua regia: AgCl, AgBr, AgI, AgCN, $BaSO_4$, $SrSO_4$, $PbSO_4$, CaF_2,† fused $PbCrO_4$, Al_2O_3, Cr_2O_3, native TiO_2 (rutile, anatase, brookite), native SnO_2 (cassiterite, tinstone), SiO_2, Si, many silicates, C, carborundum, and strongly ignited iridium (Rh, Ru, Os, Ta, Th, and some special steel alloys).

In order to bring such substances in solution it is necessary to subject them to a special treatment. The process to be chosen depends largely upon the nature of the insoluble substance, so that a few general

* The oxides of antimony are changed to Sb_2O_4 after long ignition in the air.

† Calcium fluoride will be dissolved by the long-continued action of aqua regia.

tests are necessary before going farther. Very often the preliminary examination will have been sufficient, but it is always well to perform the following simple experiments:

1. Heat a small portion of the residue insoluble in acids on the charcoal stick to see whether a metallic button can be produced.

(a) No metallic button is produced. The *absence* of **silver, lead,** and **tin** is thereby assured.

(b) A metallic button is formed. The button is flattened in an agate mortar, and its solubility in acids is tested.

(α) The metal dissolves in nitric acid forming a clear solution, showing the *absence* of **tin.** Add a little hydrochloric acid to the nitric acid solution; a curdy precipitate is formed if the metal is **silver,** consisting of silver chloride, insoluble in water, but soluble in ammonia.

If the nitric acid solution becomes turbid on the addition of sulfuric acid, **lead** is present.

(β) The metal does not dissolve in nitric acid forming a clear solution, but leaves a white, insoluble powder: **metastannic acid.** Treat a new button with concentrated hydrochloric acid, when it will dissolve completely if silver is absent. Mercuric chloride produces a white precipitate of mercurous chloride in the hydrochloric acid solution: **tin** is present.

2. Heat a second portion of the insoluble residue in a small test tube with concentrated sulfuric acid and test to see whether the escaping gas renders a drop of water turbid.

A turbidity shows the presence of an insoluble fluoride (CaF_2).

3. Heat another portion of the residue (with the help of a platinum wire) in the upper reducing flame of the gas burner, allow to cool in the inner mantle, moisten with dilute hydrochloric acid, and notice whether the odor of hydrogen sulfide can be detected. Then test to see whether it will now impart a characteristic coloration to the flame. The presence of a sulfate is betrayed by the odor of hydrogen sulfide, and the flame test shows whether barium alone or a mixture of barium, calcium, and strontium is present.

4. Test another portion of the residue in the salt of phosphorus bead; silicic acid or a silicate usually gives a skeleton bead (cf. p. 449).

Since the skeleton bead is not always obtained when silica is present, a further test for silicic acid is often necessary (cf. p. 447).

5. Now heat the salt of phosphorus bead in the reducing flame to test for the presence of **titanium,** which causes the bead to become violet. The violet color appears more quickly on the addition of a little piece of tinfoil. If iron is present at the same time, as is always true in the case of rutile, the bead is colored brownish red in the reducing flame.

6. The presence of **chromium** is often detected by the green color of the residue. In the case of chromite (gray or black residue) fuse some of the substance with sodium carbonate and potassium nitrate in the loop of a platinum wire (cf. p. 205); a yellow melt is obtained if **chromium** is present. Dissolve the melt in water, make acid with acetic acid and add silver nitrate; a reddish brown precipitate of silver chromate is obtained if chromium is present.

7. If the residue is gray or black, it may also consist of **carbon.** Heat a small portion upon a piece of platinum foil; if carbon is present, the mass will glow, and, if it does not burn completely, a lighter-colored ash will be obtained. In doubtful cases melt a little potassium chlorate in a test tube, and add a little of the insoluble residue; a distinct glowing or a little explosion will take place if carbon is present. It is necessary to avoid the addition of shreds of filter paper in this test.

8. **Silicon and Silicides** (carborundum, etc.) are seldom encountered. They show the greatest stability toward the above-mentioned reagents. By fusing with caustic alkali in a silver crucible, however, they are readily decomposed with evolution of hydrogen (cf. p. 451).

After dissolving the melt in water and acidifying, gelatinous silicic acid separates out, particularly after evaporation.

METHODS FOR ATTACKING SUBSTANCES WHICH ARE INSOLUBLE IN ALL ACIDS

1. **Insoluble Halogen Compounds** (the silver compounds alone come into consideration) can be brought into solution by melting the mass, cooling, and adding a little dilute sulfuric acid and a piece of zinc so that it comes in contact with both the acid and the insoluble substance. After a while pour off the acid; it contains the halogen acid in the presence of zinc sulfate, and should be kept for the subsequent tests for acids, cf. page 320. The residue consists of metallic silver. Wash it with water, dissolve in dilute nitric acid, filter, and test the solution for silver with hydrochloric acid.

2. **Insoluble Sulfates of the Alkaline Earths** are brought into solution by fusing in a platinum crucible with four to five times as much calcined sodium carbonate, or with a mixture of equal parts of sodium and potassium carbonates. Mix the finely powdered substance in the crucible with the sodium carbonate, cover the mixture with a thin layer of more carbonate, place the lid on the crucible, and heat at first gently over a small flame in order to drive off the moisture which the carbonate always contains, and then raise the temperature until the mass fuses to a thin liquid; maintain this temperature for about fifteen minutes. Remove the fused mass from the crucible as directed on page 448. Heat

with a little water on the water-bath until the fused mass disintegrates, and no more hard lumps can be felt with a glass rod, then filter. The filtrate will contain the sulfate as sodium sulfate, and the residue will consist of carbonates of the alkaline earths. Wash it with a 5 per cent sodium carbonate solution until no more sulfuric acid can be detected in the washings, and then wash with hot water until the wash-water no longer reacts alkaline (cf. p. 268). Dissolve the residue in acid, and analyze as described on page 275.

Although it would take repeated treatments to effect the complete decomposition of even a relatively small quantity of barium sulfate, any sulfate can be decomposed sufficiently to obtain qualitative tests for cation and anion by merely boiling the finely powdered substance with 3-normal sodium carbonate solution. Thus boiling 1 g of powdered barium sulfate with 25 ml of 3-normal sodium carbonate serves to convert about 80 per cent of the insoluble sulfate into insoluble carbonate and water-soluble sulfate:

$$BaSO_4 + Na_2CO_3 \rightarrow BaCO_3 + Na_2SO_4$$

After washing thoroughly to remove the sulfate, most of the residue will dissolve in dilute acid. The decomposition of the sulfates of lead, calcium, and strontium (also bismuth) is practically complete by this treatment.

3. **Lead Sulfate** may be boiled with a concentrated sodium carbonate solution, which forms insoluble basic lead carbonate and soluble sodium sulfate; with caustic soda, which forms soluble lead plumbite and sodium sulfate; or with ammonium acetate (cf. p. 115).

4. **Silicic Acid** and **Silicates** should be fused with sodium carbonate, or treated with sulfuric and hydrofluoric acids exactly as described on page 448.

5. **Metastannic Acid,** as obtained by the oxidation of tin with nitric acid, is readily dissolved by boiling with a little concentrated hydrochloric acid, and then treating with considerable cold water (cf. p. 175).

Tin dioxide, as it occurs in nature (tinstone), as well as the strongly ignited metastannic acid, cannot be brought into solution in this way. One of the methods mentioned on page 172 (usually the sodium carbonate and sulfur method) must be used.

6. **Insoluble Fluorides** are first heated with concentrated sulfuric acid in platinum, and any alkaline earth sulfate formed is brought into solution by the method described under 2.

7. **Titanium Dioxide** is fused with potassium pyrosulfate in a platinum or silica crucible (cf. pp. 193 and 547); or it is fused with sodium carbonate, the melt treated with cold water, and the residue dissolved in hydrochloric acid (cf. p. 547). Heating for some time with concentrated sulfuric acid will dissolve pure titanium dioxide. When cold the solution may be diluted.

Fusion with potassium pyrosulfate is also suitable for decomposing native aluminum oxide (corundum).

8. **Chromium Sesquioxide** and **Chromite** are fused with sodium carbonate and a little potassium nitrate in a platinum crucible or with sodium peroxide in a nickel or iron crucible (cf. p. 197).

9. **The Insoluble Complex Cyanides** are completely decomposed by boiling with caustic soda in a porcelain dish.

After boiling with the alkali, dilute with water and filter. The filtrate will contain the acid in the form of its sodium salt; and, in some cases, may also contain aluminum and zinc. Saturate the filtrate with carbon dioxide, boil, and filter off any precipitate ($Al(OH)_3$ or $ZnCO_3$); dissolve this precipitate in hydrochloric acid, and test for zinc and aluminum. Acidify the alkaline filtrate obtained above with hydrochloric acid, and test for ferrocyanic and ferricyanic acids according to pages 333 and 336.

The soluble complex cyanides are decomposed before the analysis by heating them with concentrated sulfuric acid (cf. p. 217).

Reactions that Accompany the Dissolving Process

When a substance is dissolved, whether in water or in acids, phenomena are often observed which may be of great importance as concerns the subsequent analysis. Moreover, the color, reaction of the solution toward indicators, or the evolution of gases will lead to important conclusions. First, test the substance with regard to its solubility in water, by taking about 0.5 g of the fine powder, adding a little cold water, and noting whether any bubbles of gas are given off.

A gas is evolved when there are present:

(*a*) **Peroxides of the Alkalies** or **Alkaline Earths**, which are partly decomposed into hydroxide and oxygen:

$$2\,Na_2O_2 + 2\,H_2O \rightarrow 4\,NaOH + O_2\uparrow$$
$$2\,BaO_2 + 2\,H_2O \rightarrow 2\,Ba(OH)_2 + O_2\uparrow$$

Barium peroxide is decomposed in this way only by heating the water.

Test the escaping gas for oxygen by means of a glowing splinter.

In the alkaline solution (red litmus is changed to blue) some undecomposed peroxide will still be found.

Dilute the solution with considerable water, cool, and carefully acidify with sulfuric acid, add a little ether and some potassium dichromate solution, and shake the mixture. If a peroxide is present, the upper ether layer will now be colored blue. A better method for detecting the hydrogen peroxide, formed by the action of the sulfuric acid upon the peroxide, consists in adding a few drops of titanium sulfate solution; a distinct yellow color will be noticed if only traces of hydrogen peroxide are present (cf. pp. 286–288).

(*b*) **Carbides of the Alkaline Earths** (calcium carbide).

These are decomposed into acetylene (which has a peculiar odor,

and burns with a luminous flame) and calcium hydroxide:

$$\mathbf{CaC_2} + 2\,H_2O \rightarrow \mathbf{Ca(OH)_2} + C_2H_2\uparrow$$

(*c*) **Nitrides of the Alkaline Earths** (magnesium nitride).

Magnesium nitride is decomposed by water into magnesium hydroxide and ammonia:

$$\mathbf{Mg_3N_2} + 6\,HOH \rightarrow 3\,\mathbf{Mg(OH)_2} + 2\,NH_3\uparrow$$

If considerable water is added, there is no gas evolution, because the ammonia will be dissolved by the water; but on boiling the solution, ammonia will be given off, which can be readily recognized by its odor.

(*d*) **Phosphides of the Alkalies and Alkaline Earths.** — These are decomposed by water, setting free spontaneously combustible phosphine:

$$2\,\mathbf{CaP} + 4\,H_2O \rightarrow 2\,Ca(OH)_2 + P_2H_4$$
$$\mathbf{Ca_3P_2} + 6\,H_2O \rightarrow 3\,Ca(OH)_2 + 2\,PH_3\uparrow$$

Very small quantities of the phosphide can be recognized by the characteristic garlic-like odor.

(*e*) **Many Chlorides, Bromides,** and **Iodides of the Negative Elements,** *e.g.*, PCl_3, PCl_5, etc., are decomposed into the halogen hydride and the oxygen acid of the negative element:

$$PCl_5 + 4\,H_2O \rightarrow 5\,HCl + H_3PO_4$$

(*f*) **A Few Sulfides Which Are Seldom Encountered** (MgS, Al_2S_3, etc.). — These are decomposed by water with loss of hydrogen sulfide, which can be detected by its odor, and by its blackening lead acetate paper:

$$\mathbf{MgS} + 2\,H_2O \rightarrow \mathbf{Mg(OH)_2} + H_2S\uparrow$$

After any reaction caused by the first addition of water is over, add about 10 to 15 ml more, heat the water to boiling, and then allow it to cool.

If the substance dissolves completely, forming a clear solution, it is evident that it is unnecessary to test for any insoluble substances in the subsequent analysis.

If a residue remains, it is possible that a part of the substance has dissolved in the water. To determine whether this is the case, decant the liquid through a filter and carefully evaporate a little of the filtrate to dryness on platinum foil (or a watch glass). If the foil is heated too hot, volatile compounds may escape unnoticed. If a residue remains after evaporation, it is evident that a part of the original substance is soluble in water. Then treat the original residue several times with small quantities of water, and analyze the aqueous extract thus obtained

by itself. Treat the part remaining undissolved with acid, using hydrochloric acid unless the preliminary examination has shown the presence of either lead or silver, when nitric acid should be used.

Treat the residue with 0.5–1 ml of 12-normal acid (notice whether there is any evolution of a gas), heat gently, and then dilute with water, to dissolve any chlorides insoluble in hydrochloric acid. It must be remembered, however, that bismuth and antimony salts form insoluble basic chlorides on dilution with water, so that too much water should not be added.

If a residue remains after treatment with acid, bring it into solution by one of the methods described on pages 467–468.

II. EXAMINATION FOR THE METALS (CATIONS)

TABLE VIII. — GENERAL SCHEME FOR SEPARATING THE METALS INTO GROUPS

<table>
<tr><td colspan="4">Solution may contain all the common basic constituents. Add HCl in slight excess. (1)</td></tr>
<tr><td>Precipitate: Group I. Examine as outlined in Table I, p. 116. (2)</td><td colspan="3">Filtrate: Groups II, III, IV, and V. Saturate with H_2S. (3)</td></tr>
<tr><td></td><td>Precipitate: Group II. Examine as outlined in Table II, p. 179. (4)</td><td colspan="2">Filtrate: Groups III, IV, and V. Test for phosphoric acid. Add NH_4OH and $(NH_4)_2S$. (5)</td></tr>
<tr><td></td><td></td><td>Precipitate: Group III. Examine as outlined in Table V, p. 251. (6)</td><td>Filtrate: Groups IV and V. Add $(NH_4)_2CO_3$. (7)</td></tr>
<tr><td></td><td></td><td></td><td>Precipitate: Group IV. Examine as outlined in Table VI, p. 275. (8)</td><td>Filtrate: Group V. Examine as outlined in Table VII, p. 295. (9)</td></tr>
</table>

PROCEDURE

1. Add HCl as directed on page 116. If the original substance was completely soluble in dilute HCl, it is evident that no silver or mercurous salt is present. Often, when lead is present, the solution is clear while hot, but lead chloride is deposited as the solution cools. It is usually best to filter off such a precipitate, but it will be changed to less soluble lead sulfide when H_2S is introduced to precipitate the second group. If the original solution is alkaline to phenolphthalein or to litmus, a precipitate may form when none of the metals of the first group is present. Thus a solution of sodium silicate gives a white, gelatinous precipitate of silicic acid, a solution of an alkali tungstate gives a precipitate of tungstic acid, a solution of a thio-salt of arsenic, antimony, or tin gives a colored sulfide precipitate and the solution of a complex cyanide may form a precipitate when neutralized. These precipitates, however, are not likely to be mistaken for a chloride of silver, lead or

mercury. If a silicate is present, it is absolutely necessary to remove the silicic acid at the start by the method given on page 446 and tungstic acid may be removed in exactly the same way. If a thio-salt is present, examine the precipitate according to Table IV, page 183, and test for alkaline earths and alkalies according to Table VI, page 275, and Table VII, page 295. If the original solution is alkaline, it is necessary to test for iron and aluminum only when the solution contains non-volatile organic matter which prevents the precipitation of these elements by hydroxide ions. The addition of HCl may cause the precipitation of BiOCl, and dilution may cause the precipitation of BiOCl, SbOCl, or a basic salt of some other metal, especially titanium and tin. With the exception of the titanium precipitate, such basic salts are easily dissolved by filtering and treating with 6-normal HCl, or the basic salts of antimony, bismuth, and tin may be changed into less soluble sulfides by introducing H_2S without filtering.

2. Examine the precipitate of Hg_2Cl_2, $PbCl_2$, and AgCl exactly as described on page 115. For the detection of thallium, which is sometimes precipitated with this group, consult Part V.

3. Transfer the filtrate from (1) to a 300-ml Erlenmeyer flask, fit the flask with a two-holed rubber stopper, and insert through one hole a right-angled glass tube which reaches nearly to the bottom of the flask and through the other hole a shorter tube, similarly bent, which reaches only to the bottom of the rubber stopper. Raise the longer tube till it is just above the surface of the solution, heat the solution to boiling and begin passing a steady stream of H_2S through the longer tube. Remove the flame from beneath the flask, close the shorter tube with a piece of rubber tubing which has one end stopped up with a short piece of stirring rod, and lower the longer tube so that it dips well below the surface of the solution. Shake well and continue keeping up the pressure of the H_2S; in this way the gas is absorbed as fast as the sulfide precipitates and the solution is kept saturated with the gas without wasting a great deal of it. When the precipitation appears to be complete, shut off the H_2S, open the flask, add an equal volume of cold water, and again saturate with H_2S. Close the short tube and shake the flask well for two or three minutes while keeping up the H_2S pressure. Finally filter off the precipitate and wash it promptly with H_2S water. If an oxidizing agent is present,* considerable free sulfur will be deposited, and this will greatly delay the precipitation of the sulfides. If it is desired to know whether a precipitate contains nothing but sulfur, wash it several times with alcohol, then with carbon disulfide (away from any free flame), and then with alcohol again; this treatment will serve to remove the sulfur. It is important to adjust the concentration of the acid properly before introducing H_2S by measuring the quantity added in getting the substance into solution and in precipitating the first group. After diluting with water, as above directed, the solution should be about 0.3-normal in acid; if more acid is present cadmium and lead sulfides will not precipitate, and if less acid is present sulfides of zinc, nickel, and cobalt may precipitate. On the whole, it is better to err with too little acid than with too much, for enough zinc, nickel, and cobalt will always remain in the filtrate to give a test in the next group and the presence of these elements does not seriously interfere with the analysis of the second group. Like cadmium, zinc gives a white ferrocyanide in the confirm-

* If much oxidizing agent or considerable arsenic acid is present, it is best to pass SO_2 into the hot solution until a complete reduction is accomplished and then remove the excess of SO_2 by a stream of CO_2. If the excess of SO_2 is not removed it reacts with H_2S chiefly as follows: $2\ H_2S + SO_2 \rightarrow 2\ H_2O + 3\ S$.

atory test for copper, and nickel gives a faint blue with ammonia; either nickel or cobalt will interfere with the final test for cadmium, but the treatment outlined on page 182 will overcome this difficulty. If after precipitating with hydrogen sulfide a turbid filtrate is obtained, due to free sulfur, prepare some filter-paper pulp by shaking pieces of filter paper in a bottle with hot water, add some of the pulp to the filtrate, and filter through a fresh filter. The hydrogen sulfide precipitate oxidizes somewhat on being exposed to the air, and a little soluble sulfate is likely to form which precipitates on coming in contact with H_2S in the filtrate. For this reason the precipitate should be washed promptly with acidulated hydrogen sulfide water without letting the filter drain completely until the washing is finished. If the filter clogs, place the filter and precipitate in a beaker, shake it up with hydrogen sulfide water, and filter through a fresh filter. In qualitative analysis, all but the first washings of a precipitate should be discarded, as a rule.

4. Examine the hydrogen sulfide precipitate as directed on page 180. If gold, platinum, or considerable tin is present, these elements are often found in the residue of mercuric sulfide obtained after treatment with nitric acid. When the presence of these elements is suspected, take a little of the residue for the mercury test and fuse the remainder in a *porcelain* crucible with a mixture of equal parts of potassium cyanide and sodium carbonate. Cool, wash out all the soluble alkali salts with water, and discard this solution. Gold, platinum, tin, and lead will be left behind in the metallic condition. Treat the metallic residue with dilute nitric acid and test the solution for lead in the regular way with sulfuric acid (p. 181). Heat the residue of gold, platinum, and metastannic acid with concentrated hydrochloric acid. Dilute, filter, and test for tin with $HgCl_2$ in the usual way (p. 185). Dissolve any gold or platinum in aqua regia, add ammonium chloride, evaporate to dryness on the water-bath, and treat the residue with a very little water; a yellow precipitate of $(NH_4)_2[PtCl_6]$ shows the presence of platinum. Filter, test with $FeSO_4$ for gold, and confirm by the charcoal stick reaction (p. 520).

5. Take a little of the filtrate from (3), boil off the hydrogen sulfide, add a little bromine water to oxidize any iron and the last traces of hydrogen sulfide, and make alkaline with ammonia. If a precipitate forms it may consist of a phosphate of barium, strontium, calcium, or magnesium, or an alkaline earth fluoride or oxalate as well as $Fe(OH)_3$, $Al(OH)_3$, etc. Phosphoric acid very often occurs in minerals, and for this reason a special procedure is often required for the analysis of Groups III and IV. Without stopping to filter off the precipitate produced by ammonia, dissolve it by the careful addition of a little nitric acid, heat the solution nearly to boiling, and add an equal volume of ammonium molybdate reagent. A yellow precipitate, which may be slow in forming, shows that phosphoric acid is present. Arsenic acid gives a similar precipitate (p. 149), but arsenic should not be present at this stage in the analysis. If phosphoric acid is found present, examine the precipitate as outlined on page 250. If an oxalate or fluoride is indicated by the preliminary examination, especially by the test with concentrated sulfuric acid, it is best to remove these acids by heating the original substance with concentrated sulfuric acid, cf. page 468. If the behavior of the original substance in the closed-tube test indicates the presence of non-volatile organic matter, it is necessary to remove it before proceeding with the analysis of Group III, because tartaric and citric acids, sugars, starches, and similar substances prevent the precipitation of iron, aluminum, and chromium with ammonia. Such organic substances can be removed by repeated treatment with concentrated sulfuric and nitric acids; add about 5 ml of sulfuric acid and an equal volume of concentrated nitric acid, and

evaporate till strong fumes of sulfuric acid are evolved, cool, and repeat the treatment with nitric acid as much as necessary. The ignition treatment often makes Al_2O_3, Cr_2O_3, Fe_2O_3, and SiO_2 insoluble. Fuse such a residue with $KHSO_4$ and examine it by itself. The treatment with sulfuric and nitric acid is likely to leave an insoluble sulfate behind; fuse it with sodium carbonate (p. 268).

6. Analyze Group III by the method on page 252. Many of the elements in this group commonly occur in different states of oxidation. In reporting the final results of the analysis it is not sufficient to state that iron, chromium, or manganese is present, but it should be stated in what condition such an element is present in the sample as received. It is necessary to determine this by special tests, using the characteristic reactions described in Part II under the element in question.

7. Treat the filtrate from (5) with $(NH_4)_2CO_3$ according to page 275.

8. Examine the $(NH_4)_2CO_3$ precipitate as directed on page 275.

9. Examine the alkali group according to the directions on page 295 for the analysis of Group V. Test a portion of the original substance for ammonium.

III. EXAMINATION FOR THE ACID CONSTITUENTS (ANIONS)

(A) Method of F. P. Treadwell*

The tests for the acid constituents (anions) are usually made after the analysis for the basic constituents (cations); the preliminary examination (heating in the closed tube and with dilute and concentrated sulfuric acid) and the solubility, combined with the knowledge of the metals that are present, indicate what acids may and what acids may not be present.

In order to avoid side reactions, the acids are usually obtained in the form of the neutral alkali salts before proceeding to test for them.

PREPARATION OF THE SOLUTION FOR THE ANALYSIS FOR ACIDS

Two cases may be distinguished:

A. The original substance contains no heavy metal (i.e., only alkalies or alkaline earths are present).

(a) **The Substance is Soluble in Water.**

Test the solution with litmus paper to see whether it is acid, alkaline, or neutral.

An Alkaline Reaction shows the possible presence of alkali cyanides, nitrites,† borates, tertiary phosphates, sulfides, thio-salts, silicates, etc.

An Acid Reaction is shown by many acid salts (cf. p. 54).

Divide the solution into two parts. If it is neutral, analyze it directly for the acids; if it is alkaline, neutralize‡ half of it with acetic acid and the other half with nitric acid; if it is acid, neutralize with sodium carbonate solution.

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* Based on Bunsen's classification of the acids (cf. p. 297).

† Perfectly pure alkali nitrites are neutral. The alkaline reaction of the commercial salts is due to the presence of alkali oxide or silicate.

‡ Thio-salts, silicates, stannites, stannates, aluminates, molybdates, tungstates, etc., may yield precipitates at this point which should be examined as described on page 472.

(*b*) **The Substance is Insoluble or very difficultly Soluble in Water, but readily Soluble in Dilute Acids.** In this case only the acids of Groups III and IV need be tested for.

Boil the dry substance with a little concentrated sodium carbonate solution and filter. The filtrate contains the acids in the form of their sodium salts.

Neutralize the solution with dilute nitric acid.

(*c*) **The Substance is Insoluble in Water and in Dilute Acids.**

The following substances may be present: $BaSO_4$, $SrSO_4$, ($CaSO_4$), CaF_2, and silicates, which often contain salts of H_3PO_4, HBO_2, H_2SO_4, HF, and HCl.

Fuse the substance with sodium carbonate in a platinum crucible, extract with water, and use the aqueous solution thus obtained for the analysis for acids, after neutralizing.

If the substance is partly soluble in water and in acids, first treat with water and then with sodium carbonate solution and fuse the residue with solid sodium carbonate. Analyze separately the three solutions thus obtained.

B. The substance contains heavy metals.

(*a*) **It is Soluble in Water** or in dilute acids, and contains no non-volatile organic matter (no carbonization in the closed-tube test).

Treat the solid substance with sufficient concentrated sodium carbonate solution to make the resulting solution weakly alkaline, and filter. If ammonium salts are present, first boil it with the solution of sodium carbonate until the vapors from the solution no longer smell of ammonia, and then filter.

Divide the resulting solution into two parts, making one part acid with acetic acid, and the other with nitric acid.

(*b*) **The Substance is Soluble in Water or Dilute Acids and Contains Non-volatile Organic Matter.** — If the metals of both the ammonium sulfide and hydrogen sulfide groups are present, pass hydrogen sulfide into the weakly acid solution until it is saturated, filter off the precipitate, add ammonia to the filtrate until it is slightly alkaline, filter again, and make this last filtrate acid with acetic acid and evaporate to a small volume. Filter off the deposited sulfur, treat the solution with solid potassium carbonate, filter if necessary, carefully acidify with nitric acid, stir vigorously, and if any potassium acid tartrate is formed, filter it off and test as described on page 383. Test the filtrate for the remaining acids.

(*c*) **The Substance is Insoluble in Strong Acids.** — Besides the salts mentioned under *A* (*c*), the following may be present: AgCl, AgBr, AgI, AgCN, $PbSO_4$, silicates (ferro- and ferricyanides).

If silver is present, the halogen acids must be looked for. Reduce the insoluble silver salt by zinc and sulfuric acid, filter off the residue, and examine the filtrate according to Table XI for HCl, HI, HBr, and HCN.

If the insoluble substance contains lead, boil it with sodium carbonate solution and filter; make the filtrate acid with hydrochloric acid, and test with $BaCl_2$ for H_2SO_4.

If silicates are present, H_3PO_4, HF, HBO_2, HCl, and H_2SO_4 must also be tested for.

In whatever way a solution is prepared, determine its behavior toward **silver nitrate and barium chloride** in order to ascertain to what groups the acids present belong.

Then make the necessary tests for the individual members.

TABLE IX. — THE SILVER NITRATE TEST

Treat the original, neutral, aqueous solution, or the solution which has been neutralized with acetic or nitric acid, with an excess of silver nitrate.

No Precipitate is Formed.	A Precipitate is Formed.			
All acids of Groups I, III, and IV are absent (cf. p. 297).	If the solution was very concentrated, the precipitate may be the silver salt of $HC_2H_3O_2$, HNO_2, or H_2SO_4. *Add water and heat.*			
	The Precipitate Dissolves.	The Precipitate Remains Undissolved.		
	All acids of Groups I, III, and IV are absent.	Acids of Groups I, III, and IV may be present. *Heat the precipitate with dilute nitric acid.*		
		The Precipitate Dissolves.	The Precipitate Does not Dissolve.	
		One or more acids of Groups III and IV is present. The acids of Group I are absent.	Present: Acids of Group I. *Filter off the precipitate and treat the filtrate drop by drop with dilute ammonia.*	
			A Turbid Zone is Formed.	No Turbid Zone is Formed.
			Present: Groups* III or IV. Yellow zone, Ag_3AsO_3, Ag_3PO_4, Red " Ag_2CrO_4, Brown " Ag_3AsO_4,† White " silver salts of H_2SO_3, $H_2C_4H_4O_6$, $H_2C_2O_4$, HPO_3, $H_4P_2O_7$.	Absent: Groups III and IV.

* Boric acid would not be precipitated in case the free acid was neutralized with ammonia. It must be tested for separately.

† It must not be forgotten that NH_4OH sometimes produces a brownish precipitate of Ag_2O in silver solutions; if the zone appears brown, shake the solution gently, which will cause the turbidity to disappear; add more NH_4OH, and with a little experience it can be determined whether the turbidity is Ag_2O or Ag_3AsO_3.

TABLE X. — THE BARIUM CHLORIDE TEST

Treat the original, aqueous, neutral solution, or the solution neutralized with acetic acid, with an excess of barium chloride solution.

No Precipitate is Formed.	A Precipitate is Formed.		
Absent: All acids of Groups III, IV, and VI.	*Add a little dilute HCl and heat the solution.**		
	The Precipitate Dissolves.	The Precipitate Remains.	
	Absent: Group VI (H_2SO_4 and HF).	Present: Group VI. *Filter off the precipitate and neutralize the filtrate with pure KOH or NaOH (free from carbonate, etc.).*	
		No Precipitate is Formed.	A Precipitate is Formed.
		Absent: Acids of Groups III and IV.	Present: Acids of Groups III and IV.

* Carbonates, sulfites, and thiosulfates will be destroyed; they must afterwards be tested for specially.

TABLE XI. — EXAMINATION OF GROUP I

*First test for HCN by placing a little of the solution on a watch-glass, adding a few drops of yellow ammonium sulfide, evaporating carefully to dryness, acidifying the dry mass with HCl, and adding a drop of $FeCl_3$ solution. If a blood-red coloration is produced, HCN is present, in which case treat a larger portion of the neutral solution with nickel sulfate * solution in excess, and filter.*

<table>
<tr><th>Precipitate.</th><th colspan="2">Solution.</th></tr>
<tr><td>$Ni(CN)_2$
Discard.</td><td colspan="2">*Treat the solution, which is now free from hydrocyanic acid, with a little caustic soda solution (free from halogen), boil and filter off the precipitate of $Ni(OH)_2$, divide the filtrate into two parts and use one part for the HBr and HI tests and the other for the HCl test.*</td></tr>
<tr><td></td><td>Tests for HI and HBr.</td><td>Test for HCl.</td></tr>
<tr><td></td><td>*Make the solution acid with dilute H_2SO_4, add chlorine water drop by drop, and shake the solution with CS_2 or $CHCl_3$. If the latter is colored violet, HI is present. By further addition of chlorine water, the CS_2 or $CHCl_3$ is decolorized completely if HBr is absent, but turned yellowish-brown if HBr is present. If too much chlorine water is used a wine-yellow color is produced.*</td><td>*Make the solution slightly acid with HNO_3, and add dilute $AgNO_3$ drop by drop. AgI and AgBr are first precipitated (yellow). Filter and add more $AgNO_3$. If the precipitate still appears yellow, filter through a new filter, and again add $AgNO_3$ to the filtrate until a white precipitate of AgCl is formed if HCl is present.*</td></tr>
</table>

* If ferricyanic acid is present also add a little ferrous sulfate. Ferrocyanic acid is completely precipitated by nickel sulfate.

Group II

The members of this group are almost always detected in the preliminary examination. The special tests for these acids are described on page 345 *et seq.*

Group III

SO_2, CO_2, $H_2C_2O_4$ are recognized in the preliminary examination. HPO_3, $H_4P_2O_7$, HBO_2, and $H_4C_4H_4O_6$ are tested for separately by the special reactions described on page 365 *et seq.*

Group IV

CrO_3, H_3PO_4, and $H_2S_2O_3$ are detected in the preliminary examination, and in the analysis for metals.

Group V

$HClO_3$ and HNO_3 are usually detected in the preliminary examination. Their presence is, however, always confirmed by the procedure described on page 424.

Groups VI and VII

These acids are usually detected in the preliminary examination. Their presence is confirmed by the tests described under H_2SO_4, HF, and SiO_2.

(B) Method of A. A. Noyes*

According to this simplified method of testing for the common acidic constituents likely to be present in minerals and commercial products, the substances are classified into (1) natural substances and igneous products and (2) non-igneous products.

The first class includes minerals, ores, slags, mattes, glasses, porcelains, abrasives, and other ceramic products. These substances are examined for borate, carbonate, chloride, cyanide, fluoride, phosphate, silicate, sulfide, and sulfate. The second class includes such industrial products as ordinary chemicals, pigments, fertilizers, and commercial preparations which are not high-temperature products. These substances are tested for arsenate, arsenite, borate, bromide, carbonate, chlorate, chloride, chromate, cyanide, ferrocyanide, ferricyanide, fluoride, hypochlorite, iodide, nitrate, nitrite, oxalate, phosphate, silicate, sulfate, sulfide, sulfite, and thiocyanate.

Phosphate and silicate are detected during preparation of the solution and examination for basic constituents.

ANALYSIS OF NATURAL SUBSTANCES AND IGNEOUS PRODUCTS

TABLE XII.—DETECTION OF SULFATE, CARBONATE, SULFIDE, AND CYANIDE

Boil 0.5 *g of the substance with HCl and Zn, collecting* 3 *ml of distillate in* $Ba(OH)_2$ *solution; filter the mixture left in the distilling flask.* (1)

Filtrate: *Add* $BaCl_2$. White precipitate of $BaSO_4$ shows sulfate. (2)	Distillate: A white precipitate of $BaCO_3$ shows carbonate. The solution may contain dissolved BaS and $Ba(CN)_2$.	
	To a part of the solution add $HC_2H_3O_2$ *and* $Pb(C_2H_3O_2)_2$. A black precipitate of PbS shows sulfide. (3)	*To the rest of the solution add* $FeCl_2$, *boil and add HCl.* The formation of Prussian blue shows cyanide. (3)

PROCEDURE

1. Place 0.5 g of the finely powdered substance, about as much granulated zinc, and 10 ml of 3-normal HCl, which has just been boiled for a minute in a test tube, in the 50-ml flask *A* of Fig. 17. Both the flasks shown in the drawing are made of

* *Qualitative Chemical Analysis*, 8th Edition, 1920. This method of analysis is well suited for the use of large classes with a limited time assigned for the study of the subject.

hard glass. The safety tube *B* is about 25 cm long and reaches nearly to the bottom of *A*. The delivery tube *C* is about 50 cm long and extends only to the bottom of the rubber stopper in *A* but nearly to the bottom of flask *D* which rests in a beaker of cold water and contains 25 ml of barium hydroxide solution. Both flasks are provided with two-holed rubber stoppers, but one of the holes is left open in the flask *D*.

Heat the mixture in the flask *A* and slowly distil about 3 ml of liquid into *D*. Examine the liquid that remains in *A* by § 2 and the liquid in *D* by § 3.

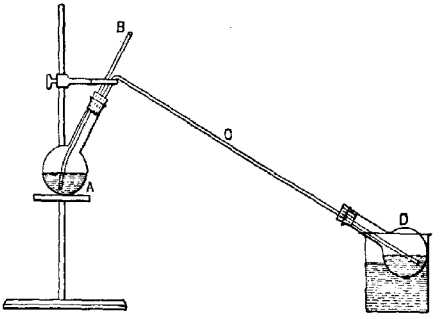


FIG. 17

2. Filter the contents of flask *A*, and add barium chloride to the filtrate. *A white precipitate of barium sulfate shows the presence of sulfate.*

3. Take two-thirds of the liquid in the flask *D* and add acetic acid, 1 ml at a time, until the solution reddens blue litmus paper. A white precipitate of $BaCO_3$ which dissolves partly or completely upon adding the acid shows that a carbonate is present. If only a slight turbidity is obtained, compare it with the result obtained by carrying out the distillation test with acid and zinc alone.

Add 5 ml of lead acetate solution: *a black precipitate of PbS shows the presence of a sulfide.* In doubtful cases a blank test must be made with the acid and zinc alone, carrying out the distillation in exactly the same manner.

Test the remainder of the distillate for cyanide by adding 1 ml of $FeCl_2$ solution, boiling for a minute, and finally making acid with HCl. *The formation of Prussian blue shows the presence of a cyanide.*

4. Place 1 g of finely powdered substance, 3 ml of water, and 3 ml of concentrated H_2SO_4 in the distilling flask *A* of Fig. 17 and pour 5 ml of water into flask *D*. Distil until the liquid in *A* becomes oily in appearance and the flask is filled with white fumes. During the distillation take away the flame from under the flask for a moment, to allow the liquid in the safety-tube to run back into the flask; do this twice. Test the distillate for chloride and fluoride as described in § 5. After the solution in the distilling flask has cooled to room temperature, add to it 8 ml of methyl alcohol and mix by shaking. Distil off most of the alcohol, catching the distillate in 8 ml of 12-normal HCl diluted with 3 ml of water. Examine this second distillate by § 6.

5. Boil the first distillate obtained by § 4 for about a minute, and filter if it is turbid. To about one-fourth of it add 2 ml of 6-normal HNO_3 and a little $AgNO_3$

TABLE XIII. — DETECTION OF CHLORIDE, FLUORIDE, AND BORATE

Distil 1 *g of the substance* (A) *with* H_2SO_4 *alone and* (B) *with* H_2SO_4 *and* CH_3OH. (4)

A. *Test a portion of the first distillate with* $AgNO_3$. A white precipitate of AgCl shows the presence of a chloride. *Test another portion with* $CaCl_2$. A white precipitate of CaF_2 shows the presence of fluoride. (5)	B. *Test the second distillate with HCl and turmeric solution.* An orange or red color shows borate. (6)

solution. *A white precipitate of AgCl* shows the presence of chloride. To the remainder of the distillate add 5 ml of $CaCl_2$ solution and allow the mixture to stand fifteen minutes. *A while precipitate of* CaF_2 *shows the presence of fluoride.* Confirm by the Daniel test described on page 437.

6. Transfer the second distillate of § 4 to a graduate, dilute to 20 ml, and add 2 drops of alcoholic turmeric solution (cf. p. 91). *An orange or red color shows the presence of borate* (cf. p. 376).

TABLE XIV. — DETECTION OF SULFATE, FLUORIDE, BORATE, AND SILICATE IN SUBSTANCES UNDECOMPOSED BY ACIDS

Fuse the substance with Na_2CO_3 *and extract the melt with water, rejecting the insoluble residue. Divide the solution into two portions.* (7)

Take two-thirds of the aqueous extract and evaporate to about 6 ml. Add HCl, filter, reject the precipitate and add $BaCl_2$ *to the filtrate. Filter.* (8)		*To the remainder of the aqueous extract add HCl and evaporate to dryness. Add HCl to the residue, dilute and filter.* (10)	
Precipitate: A white precipitate of $BaSO_4$ shows sulfate.	Filtrate: *Add* $NaC_2H_3O_2$ *and* $CaCl_2$. A white precipitate of CaF_2 shows fluoride. (9)	A gelatinous precipitate of H_2SiO_3 shows silicate. (11)	*Test the filtrate for borate with alcoholic turmeric solution.* A red or orange color shows borate. (12)

7. If the original substance is not decomposable by treatment with mineral acids in an open dish, or an insoluble residue is left after such treatment, the above-described tests for sulfate, fluoride, and borate are likely to give negative results even when these acid constitutents are present. Fuse 1 g of the original substance, or the residue insoluble in acids, with 6 times as much anhydrous sodium carbonate in a 30-ml nickel crucible over a Méker burner. Protect the contents of the crucible from the combustion products of the illuminating gas by keeping the crucible covered and by placing it in a hole in a sheet of asbestos paper, fitted tightly so that the asbestos paper comes only a little below the upper edge of the crucible. After the fusion, cool the crucible and place it in 40–60 ml of water. Boil until the fused mass

is disintegrated, and filter. Reject the insoluble residue, or use it for tests for basic constituents.

8. Evaporate two-thirds of the aqueous extract to about 6 ml and add 6-normal HCl, 10 drops at a time, until the stirred solution is acid to litmus. Filter and reject any precipitate. Add 1 ml of HCl to the filtrate and a little $BaCl_2$ solution. *A white precipitate of $BaSO_4$ shows the presence of sulfate.* Since illuminating gas contains a little sulfur, sometimes a slight turbidity is due to this source. In doubtful cases a blank test should be made by fusing the same quantity of sodium carbonate in the nickel crucible without any of the substance to be tested.

9. Filter off any barium sulfate obtained in § 8 and test with more $BaCl_2$ to make sure that the precipitation of sulfate was complete. Add 10 ml of 3-normal $NaC_2H_3O_2$ solution and 10 ml of $CaCl_2$ reagent. *A white precipitate of CaF_2 forming within fifteen minutes shows the presence of fluoride.* Confirm as in § 5.

10. Make the remainder of the aqueous extract obtained in § 7 slightly acid with HCl and test for silicate as described on page 447.

11. Filter off any silicic acid obtained in § 10 and test the filtrate with 5 ml of 12-normal HCl, 8 ml of C_2H_5OH, and 2 drops of alcoholic turmeric solution as in § 6.

ANALYSIS OF NON-IGNEOUS COMMERCIAL PRODUCTS

TABLE XV. — PREPARATION OF THE SOLUTION, GROUP TESTS

Boil 2.5 g of the fine powder with 3-normal Na_2CO_3 solution, filter, and wash the residue. Examine if for sulfide as in Table XII. Use separate portions of the solution for the tests outlined below and in Tables XVI–XX.

A	B	C	D
Add $AgNO_3$, $NaNO_2$ and HNO_3. A precipitate shows the presence of a member of the CHLORIDE GROUP. *Examine for* S^{--}, CN^-, $[Fe(CN)_6]^{==}$, $[Fe(CN)_6]^{---}$, SCN^-, Cl^-, Br^-, I^-, ClO^- *and* ClO_3^- *by* Tables XVI, XVII, and XVIII.	*Add $HC_2H_3O_2$, $BaCl_2$ and $CaCl_2$.* A precipitate shows the presence of one or more members of the SULFATE GROUP. *Test for* SO_4^{--}, SO_3^{--}, CrO_4^{--}, F^- *and* $C_2O_4^{--}$ *by Table* XIX.	*Add $MnCl_2$ and HCl.* A dark color of $MnCl_2$ shows the presence of an OXIDIZING ACIDIC CONSTITUENT. If it is not obtained, further tests for $[Fe(CN)_6]^{---}$, ClO^-, ClO_3^-, CrO_4^{--}, NO_3^- and NO_2^- are unnecessary.	*Add HCl, $FeCl_3$ and $K_3[Fe(CN)_6]$.* The formation of Prussian blue indicates the presence of a REDUCING ACID CONSTITUENT. If it is not obtained further tests for S^{--}, $[Fe(CN)_6]^{==}$, I^-, SO_3^{--} and NO_2^- are unnecessary.

PROCEDURE

Gently boil 2.5 g of the finely powdered substance with 25 ml of 3-normal Na_2CO_3 in a covered porcelain dish. Filter and wash the residue with hot water, and test it for sulfide only, by the method outlined in Table XII. Dilute the aqueous extract to 30 ml and use portions of it for the tests *A*, *B*, and *C* below for further tests according to Tables XVI–XX.

A. To 1 ml of the Na_2CO_3 solution, add 5 ml of water, 3 drops of chloride-free, 3-normal $NaNO_2$ solution, 1 ml of $AgNO_3$ reagent, and 2 ml of 6-normal HNO_3. If

a precipitate of insoluble silver salt is formed, continue as outlined in Table XVI.

B. Dilute 2 ml of the Na_2CO_3 solution with an equal volume of water, add 6-normal $HC_2H_3O_2$, 5 drops at a time, until the stirred solution is acid to litmus paper, and add as much more acid in excess. Filter if necessary, and add 1 ml of $BaCl_2$ reagent and 3 ml of $CaCl_2$ reagent. Heat to boiling and allow to stand ten minutes. If a precipitate forms of insoluble barium or calcium salt, test another portion of the $NaCO_3$ solution by the method outlined in Table XIX.

C. To 1 ml of the Na_2CO_3 solution, add 4 ml of a saturated solution of $MnCl_2$ in concentrated HCl and heat nearly to boiling. A dark brown or black color of $MnCl_3$ shows that a nitrate, nitrite, chlorate, hypochlorite, permanganate, chromate, or ferricyanide is present. If the test is not obtained, these acids are absent.

D. To 1 ml of the Na_2CO_3 solution add 3 ml of water, 1 ml 6-normal HCl, 2 drops of $FeCl_3$ reagent, and 2 drops of $K_4[Fe(CN)_6]$ reagent. A blue or green coloration (Prussian blue) indicates the presence of sulfide, ferricyanide, iodide, sulfite, or nitrite. If it is not obtained these acid constituents are not present in the Na_2CO_3 solution.

If a positive indication was obtained in *C*, test a 2-ml portion of the Na_2CO_3 solution for nitrate and nitrite by Table XX. In all cases examine a 3-ml portion of the Na_2CO_3 solution for borate according to Table XX. If arsenic was found present in the examination for cations, examine a 3-ml portion of the Na_2CO_3 solution for arsenite and arsenate by Table XX.

TABLE XVI. — SEPARATION OF THE CHLORIDE GROUP INTO SUBGROUPS

To 6 ml of Na_2CO_3 solution (Table XV) add $Pb(NO_3)_2$ and filter if necessary. (1)

Black precipitate of PbS shows sulfide.	Filtrate: *Add $HC_2H_3O_2$ and $Ni(NO_3)_2$ solution.* (2)		
	Precipitate: $Ni_3[Fe(CN)_6]$, $Ni_2[Fe(CN)_6]_2$, $Ni(CN)_2$. See Table XVII.	Filtrate: may contain SCN^-, I^-, Br^-, Cl^-, ClO_3^-. *Add $AgNO_3$ and HNO_3.* (3)	
		Precipitate: AgSCN, AgI, AgBr, AgCl. See Table XVIII.	Filtrate: may contain ClO_3^-. *Add $NaNO_2$. A white precipitate of AgCl indicates chlorate or hypochlorite.* (4)

1. If $AgNO_3$ produced a precipitate by the procedure given in Table XV, the color of the precipitate often shows which member of this group is present. Thus Ag_2S is black, AgI is yellow, AgBr is light yellow, $Ag_3[Fe(CN)_6]$ is orange, and AgCl, Ag(CN), AgSCN, and $Ag_4[Fe(CN)_6]$ are white. The white precipitates darken, however, on exposure to light. To test systematically for the various members of the chloride group, proceed as follows:

Add 5 ml of water and 1 drop of normal $Pb(NO_3)_2$ solution to 6 ml of the Na_2CO_3 solution. *If a gray or black precipitate of PbS is formed, sulfide is present.* A white precipitate of basic lead carbonate shows that sulfide is absent. Filter off the precipitate and reject it.

2. Add 6-normal $HC_2H_3O_2$ to the filtrate, 10 drops at a time, until the stirred solution is acid to litmus, and then one-third as much more of the acid. Filter off any precipitate and reject it. To the solution add 3–10 ml of normal $Ni(NO_3)_2$ solution and allow the mixture to stand 10 minutes with frequent shaking. If a precipitate of $Ni(CN)_2$, $Ni_2[Fe(CN)_6]$, or $Ni_3[Fe(CN)_6]_2$ forms filter it off, wash it thoroughly with water, and examine it according to Table XVII. If the precipitate is so slimy that it is hard to filter, add some filter paper pulp, shake vigorously for a minute or two, and filter with gentle suction.

3. To the filtrate from § 2, add 2 ml of 6-normal HNO_3 and some $AgNO_3$ solution. If a black precipitate of Ag_2S forms, owing to the addition of an insufficient quantity of lead salt, add 5 ml more of HNO_3 and boil gently for a minute or two. A white precipitate indicates the presence of a chloride or thiocyanate, a yellow precipitate indicates an iodide or bromide. Filter and examine the precipitate by Table XVIII and the filtrate by the following treatment, if an oxidizing constituent was found in Test *C* of Table XV.

4. Add a few drops more of $AgNO_3$ solution and 5 to 20 drops of chloride-free, 3-normal $NaNO_2$ solution. A white precipitate of AgCl indicates the presence of a chlorate or hypochlorite. Since hypochlorite is changed into chloride and chlorate by boiling with Na_2CO_3 it is necessary to test the original substance for chlorate and hypochlorite.

Treat 0.5 g of the original substance with 10 ml of cold water, shake, and filter. To one-half of the filtrate add 6-normal $HC_2H_3O_2$, a few drops at a time, until the solution is acid. Then add 3 ml of $Pb(C_2H_3O_2)_2$ reagent, heat to boiling, and allow to stand five minutes. A brown precipitate of PbO_2 shows that hypochlorite is present (cf. p. 308). In case a positive test for hypochlorite is obtained, to the other half of the aqueous solution add 20 ml more of water, 5 ml of HNO_3 and 5 ml of normal, chloride-free $NaAsO_2$ solution, and 5 ml of $AgNO_3$ reagent. The sodium arsenite reduces the hypochlorite to chloride without affecting the chlorate. Filter off the silver chloride and reduce any chlorate in the filtrate with $NaNO_2$ solution. A white precipitate of silver chloride now shows the presence of chlorate. It is so difficult

TABLE XVII. — DETECTION OF THE SEPARATE CYANIDES

Treat the nickel precipitate of Table XVI on the filter with 3-normal NH_4OH. To the solution thus obtained, which may contain $[Ni(NH_3)_4](OH)_2$, $(NH_4)_4[Fe(CN)_6]$ $(NH_4)_2[Fe(CN)_6]$, and NH_4CN, *add* $AgNO_3$ and Na_2SO_3. (5)

<table>
<tr><td rowspan="3">Precipitate: $Ag_4[Fe(CN)_6]$. Add HCl and $Fe(NO_3)_3$. A blue residue of Prussian blue (and white AgCl) shows ferrocyanide or ferricyanide. (6)</td><td colspan="3">Filtrate: $NH_4[Ag(CN)_2]$, $Ni(NO_3)_2$, $AgNO_3$ and NH_4NO_3. Add HNO_3.</td></tr>
<tr><td colspan="3">Precipitate: AgCN, add $(NH_4)_2S$. (7)</td></tr>
<tr><td>Residue: Ag_2S. Reject.</td><td>Solution: NH_4CNS. Add $Fe(NO_3)_3$. Red color shows cyanide. (8)</td><td>Filtrate: Ni^{++}, Ag^+ and NH_4^+ as nitrates. Reject.</td></tr>
</table>

to get reagents free from chloride that often a turbidity is obtained here when no chlorate is present. The behavior of a chlorate with concentrated sulfuric acid is characteristic and should always be used as a confirmatory test for chlorate (cf. p. 423).

5. Pour a 10-ml portion of 3-normal NH_4OH three times through the precipitate of insoluble nickel salt obtained according to Table XVI. To the ammoniacal solution, add 2–5 ml of $AgNO_3$ and normal Na_2SO_3 solution, a few drops at a time and shaking after each addition, until any brown color disappears. If a precipitate forms, examine it by § 6 and the remaining solution by § 7.

6. *A white precipitate of $Ag_4[Fe(CN)_6]$ shows that ferrocyanide or ferricyanide was present in the original substance.* Treat the precipitate on the filter with 1 ml of 6-normal HCl mixed with an equal volume of normal $Fe(NO_3)_3$ solution. The formation of Prussian blue confirms the last conclusion. To determine whether ferrocyanide or ferricyanide was originally present, dilute 1 ml of the original Na_2CO_3 solution (Table XV) with 5 ml of water and add 1 ml of 6-normal HNO_3 and 1 ml of normal $Fe(NO_3)_3$ solution. *The formation of Prussian blue shows the presence of ferrocyanide.* Filter, repeatedly if necessary, and add 1 ml of $FeCl_3$ solution. *The formation of Prussian blue now shows that a ferricyanide was present.*

7. To the filtrate from the insoluble $Ag_4[Fe(CN)_6]$ obtained in § 5, add HNO_3 until the odor of NH_3 disappears and then 5 ml more of acid. *The formation of a white precipitate indicates the presence of a cyanide.* Filter and reject the filtrate.

8. Pour repeatedly through the filter a 5-ml portion of $(NH_4)_2S$ reagent, evaporate the solution just to dryness, and add to the residue 2 ml of HCl and 2 ml of $Fe(NO_3)_3$ solution. A red color of ferric thiocyanate confirms the cyanide test (cf. p. 327).

TABLE XVIII. — DETECTION OF THIOCYANATE, IODIDE, BROMIDE AND CHLORIDE

Silver Precipitate from Table XVI, § 3: AgSCN, AgI, AgBr, AgCl. *Treat with NH_4OH and $(NH_4)_2S$.* (9)

Residue: Ag_2S.	Solution: may contain SCN^-, I^-, Br^- and Cl^- as ammonium salts. *Add HNO_3, $Fe(NO_3)_3$ and CCl_4. Shake* and allow two layers to form. (10)				
	CCl_4 layer: Purple color shows iodide.	Water layer: Br^-, Cl^-, $Fe(SCN)_3$ and some I_2. Red color shows thiocyanate. *Boil off iodine, cool, add $KMnO_4$ and CCl_4.* (11)			
		Vapor: I_2.	CCl_4 layer: Br_2. Orange color shows bromide.	Water layer: *Boil off all of Br_2 add $NaNO_2$ and $AgNO_3$.* (12)	
				Vapor: Br_2.	Precipitate: AgCl shows chloride.

9. Transfer the precipitate of insoluble silver salt (Table XVI, § 3) to a small porcelain dish and digest it with 5 ml of concentrated NH_4OH. Add $(NH_4)_2S$, 10 drops at a time, until after heating the mixture nearly to boiling and letting the precipitate settle, the reagent causes no further precipitation of silver sulfide. Filter, and reject the precipitate.

10. Evaporate the filtrate until it no longer smells of ammonia, add 5 ml of water, and filter off any precipitate. Pour the solution into a small separatory funnel, add 1 ml of 6-normal HNO_3, 3–8 ml of normal $Fe(NO_3)_3$ solution, and 1 ml of CCl_4. Shake the mixture well and allow it to settle. *A purple color of the lower layer shows that an iodide was present* (cf. p. 319). If an iodide is absent, pass at once to § 11. *A red color of the aqueous layer shows presence of thiocyanate or much iodide.*

If iodide is present, draw off the CCl_4 layer, add 3 ml of fresh CCl_4, and shake. Draw off the bottom liquid, and repeat these operations until the CCl_4 no longer shows a purple color. Transfer the aqueous solution to a porcelain dish and boil for one minute. Pour back into the separatory funnel, add 1 ml of CCl_4, and shake. *A red color of the aqueous solution shows thiocyanate.*

11. Add to the mixture in the separatory funnel, 2 ml of 6-normal HNO_3 and then 0.2-normal $KMnO_4$, 2 drops at a time, until the aqueous layer shows the purple color of permanganate. Shake and allow the two liquids to settle. *A yellow or orange color in the CCl_4 layer shows the presence of bromide.*

TABLE XIX. — DETECTION OF SULFATE, SULFITE, CHROMATE, FLUORIDE, AND OXALATE

To 6 ml of Na_2CO_3 solution (Table XV) *add* $AgNO_3$ *solution if sulfide was found by* § 1 *or thiocyanate by* § 10. *Acidify with HCl and filter if necessary. Add* $BaCl_2$. (13)

<table>
<tr><td rowspan="5">Precipitate: $BaSO_4$ shows sulfate.</td><td colspan="3">Filtrate: may contain SO_3^{--}, $Cr_2O_7^{--}$, F^-, $C_2O_4^{--}$. Add Br_2 solution. (14)</td></tr>
<tr><td rowspan="4">Precipitate: $BaSO_4$ shows sulfite.</td><td colspan="2">Filtrate: may contain $Cr_2O_7^{--}$, F^-, $C_2O_4^{--}$. Add $NaC_2H_3O_2$ and $CaCl_2$. (15)</td></tr>
<tr><td colspan="2">Yellow precipitate: $BaCrO_4$.
White precipitate: CaF_2, CaC_2O_4.</td></tr>
<tr><td>Test a part of the precipitate for fluoride by the Daniel test on page 437. (16)</td><td>Dissolve a part of the precipitate in HNO_3, add $KMnO_4$ and distill, catching the vapors in $Ba(OH)_2$ solution. A white precipitate of $BaCO_3$ shows oxalate. (17)</td></tr>
</table>

12. Transfer the aqueous solution to a flask; dilute to about 40 ml with water. If bromide or thiocyanate has been found, boil the mixture for five minutes, adding more $KMnO_4$ if the mixture loses its purple color. Add 3-normal, chloride-free $NaNO_2$ solution until the mixture is decolorized and any precipitate manganese

dioxide has dissolved. Then add a little $AgNO_3$. *A white precipitate of silver chloride shows the presence of chloride.*

13. If a precipitate was obtained in the procedure of Table XV *B*, take 6 ml of the original Na_2CO_3 solution (Table XV), and, if sulfide or thiocyanate has been found present by § 1 or § 10, add an excess of $AgNO_3$ solution. If these acidic constituents are not removed some sulfate will be formed in § 14 when bromine is added. Filter and make the filtrate slightly acid by adding HCl, 10 drops at a time. Filter off and reject any precipitate of silver chloride. Add 1 ml more of HCl and 5 ml of $BaCl_2$ solution. *A white precipitate of $BaSO_4$ shows sulfate.*

14. Filter off any $BaSO_4$ and add saturated bromine water, 1 ml at a time, until the liquid after shaking smells of it. Heat nearly to boiling. *A white precipitate of $BaSO_4$ shows sulfite.* Filter off the precipitate.

15. To the filtrate add 10 ml of 3-normal $NaC_2H_3O_2$ solution and 10 ml of normal $CaCl_2$ solution. A yellow precipitate shows chromate. A white precipitate may be fluoride or oxalate. Shake well and pour one-half of the mixture through each of two filters, rejecting the filtrates. Wash the precipitates well with water.

16. Treat one portion of the precipitate as outlined on page 437 to determine whether fluoride is present.

17. Treat the other portion of the precipitate to determine the presence of oxalate as follows: Pour a 5-ml portion of hot, 6-normal HNO_3 several times through the filter and transfer the solution to the flask *A* of Fig. 17. Add 5 ml of 0.2-normal $KMnO_4$ which has been previously made acid with HNO_3 and heated to boiling. Boil the contents of the flask for two or three minutes and catch the distillate in 25 ml of $Ba(OH_2)$ solution. *A white precipitate of $BaCO_3$ shows oxalate* (cf. p. 380).

TABLE XX. — DETECTION OF NITRATE, NITRITE, BORATE, ARSENATE, AND ARSENITE

Use the sodium carbonate solution obtained according to Table XV for these tests.

<table>
<tr><td rowspan="2">If an oxidizing acidic constituent was found according to Table XV, C, boil 2 ml of the solution with NaOH and Al. Test the vapors for NH_3 with K_2HgI_4. A red precipitate of $HgO \cdot HgNH_2I$ shows nitrite or nitrate. (18)</td><td rowspan="2">If a test for either nitrite or nitrate was obtained, add $HC_2H_3O_2$ and CSN_2H_4. Evolution of N_2 and formation of red $Fe(SCN)_3$ on adding $FeCl_3$ shows nitrite. (19)</td><td rowspan="2">Add HCl, C_2H_5OH and turmeric solution. An orange color shows borate. (20)</td><td colspan="2">Add HNO_3, NH_4OH and $Mg(NO_3)_2$. (21)</td></tr>
<tr><td>Precipitate: $MgNH_4AsO_4$. Add $AgNO_3$ solution. A red residue of Ag_3AsO_4 shows arsenate. (22)</td><td>Filtrate: may contain AsO_3^{---}. Introduce H_2S. A yellow precipitate of As_2S_3 shows arsenite. (23)</td></tr>
</table>

18. If a positive test with $MnCl_2$ reagent was obtained, test for nitrate or nitrite to see if ammonia can be formed by reduction with aluminum in alkaline solution. If the original substance contains ammonium, boil 2 ml of the sodium carbonate solution, obtained as outlined in Table XV, with 10 ml of water and 3 ml of 6-normal

sodium hydroxide until the volume of liquid has been reduced one-third. If no ammonium salt is present in the original substance, this boiling is unnecessary unless the sodium carbonate solution has stood for some time in the laboratory. To the cold alkaline solution containing Na_2CO_3 and NaOH, add about 0.5 g of aluminum turnings and heat gently so as to keep up a brisk evolution of hydrogen Hold in the vapors a glass rod wet with Nessler solution. *An orange or red precipitate on the rod shows the presence of nitrate or nitrite.*

To estimate the quantity of nitrate or nitrite carry out the test so that the escaping vapors pass into a test tube containing 5 ml of cold water, which is kept cool by placing it in a beaker of water. To the distillate add Nessler solution until no more precipitate is formed and compare the quantity of precipitate with that produced in solution of ammonium chloride containing a known quantity of the salt.

19. If a positive test was obtained in 18, take another 1-ml portion of the original Na_2CO_3 solution and add gradually 1 ml of 6-normal acetic acid. (If thiocyanate or iodide has been found present, shake 1 ml of the sodium carbonate solution with about 0.5 g of solid Ag_2CO_3 and filter.) Add 1 ml of 6-normal acetic acid and an equal volume of a 10 per cent solution of thiourea. Let the mixture stand five minutes. *The formation of gas bubbles indicates a nitrite.* Add 1 ml of HCl and 1 ml of $Fe(NO_3)_3$ solution. *A red color proves that nitrite is present.* If no red color is obtained, a nitrate is present. (In this scheme of analysis no provision is made for detecting a nitrate in the presence of a nitrite. Cf. p. 420.)

20. To just 3 ml of the original sodium carbonate solution, add just 8 ml of 12-normal HCl in small portions. Add 8 ml of ethyl alcohol, allow the sodium chloride to settle out, and decant the solution into another test tube. Add, from a dropper, just 2 drops of turmeric dissolved in ethyl alcohol and allow the mixture to stand ten minutes. *An orange or red color shows the presence of borate.* Compare the color with that obtained with a known quantity of sodium borate.

Chlorate, nitrate, nitrite, and chromate affect the color of turmeric, and when iodide is present there is sometimes trouble caused by the liberation of iodine during this test. If any of these interfering constituents are present, evaporate 3 ml of the sodium carbonate solution to dryness, add carefully 2 ml of 12-normal HCl, and again evaporate to dryness. To the residue add 1 ml of 3-normal Na_2CO_3 solution and 2 ml of water, heat to boiling, and filter if necessary. Then apply the borate test as described above. During this treatment a part of the boric acid will be lost by volatilization.

21. If arsenic was found present in the examination for cations, dilute 5 ml of the Na_2CO_3 solution with twice as much water and add HNO_3, 1 ml at a time, until an acid reaction is obtained. Then add 6-normal NH_4OH a few drops at a time until the stirred mixture turns red litmus blue, avoiding an excess. Filter if necessary, and add 10 ml of $Mg(NO_3)_2$ reagent. Let the mixture stand ten minutes with frequent shaking. Filter and wash any precipitate with normal NH_4OH. *A white precipitate of $MgNH_4AsO_4$ shows the presence of arsenate if phosphate is absent.* Test the filtrate with H_2S to see if it contains any arsenic in the trivalent condition. An immediate precipitation of yellow As_2S_3 shows the presence of arsenite.

Pour onto the filter containing the insoluble magnesium salt a 1-ml portion of $AgNO_3$ solution to which a few drops of acetic acid have been added. A dark red residue shows the presence of arsenate. If the residue is yellow and there is doubt whether any arsenate is present, pour a 5-ml portion of 6-normal HCl through the filter a number of times and add 1 ml of KI solution and 1 ml of CCl_4. Shake, and if the carbon tetrachloride becomes purple, an arsenate is present. (Cf. p. 150.)

If a precipitate of doubtful color was obtained in the As_2S_3 test, examine the precipitate for arsenic as outlined in Table IV, page 183.

Detection of Carbonate and Sulfide in the Original Substance. Test as described under Table XII, § 3.

B. The Substance is a Metal or an Alloy

The analysis of a metallic alloy is much simpler than that of a mixture of salts, because there are no acids to test for. Of the electronegative elements, usually only phosphorus, silicon, carbon, and sulfur have to be considered.

Since all common metals, with the exception of gold, platinum, tin, and antimony, are soluble in nitric acid, alloys are usually brought into solution by dissolving therein, and the use of aqua regia is necessary in only a few cases. Many alloys rich in silicon (*e.g.*, copper silicide) are extremely difficultly soluble even in aqua regia, and are best brought into solution by fusing with caustic alkali in a silver crucible, and afterwards dissolving the melt in nitric acid.

It is not advisable to dissolve an alloy in hydrochloric acid, for phosphides, carbides, silicides, sulfides, and arsenides, which are often present in small amounts, are decomposed by this acid in such a way that the negative elements are evolved as hydrogen compounds, and thus escape detection. For the analysis of ordinary alloys, the following procedure is used:

Place 1 or 2 g of the alloy (best in the form of borings) in a 200-ml porcelain dish and treat them under a good hood with about 20 ml of nitric acid, density 1.25–1.30 (1 vol. conc. HNO_3 + 1 vol. H_2O). After the first violent reaction is over, carefully evaporate (with constant stirring) almost to dryness, being careful to avoid overheating;* add a little water, and heat.

(*a*) The mass dissolves completely. The alloy contains neither tin nor antimony; analyze it according to Table XXI, page 491.

(*b*) The mass does not dissolve completely, but a white, greenish residue remains; analyze according to Table XXII, page 492.

C. The Substance is a Liquid

The color, odor, and reaction towards litmus enable one to draw important conclusions.

(*a*) The solution reacts neutral; it contains no free acid, free base, acid salt, no salt which shows an acid or alkaline reaction on account of hydrolysis, nor any insoluble salt.

First of all, determine whether there are any solid substances dissolved in the liquid by evaporating a small portion to dryness at as low a temperature as possible (so as not to lose any volatile substances). If a residue remains, examine it according to A, page 453.

(*b*) The solution reacts alkaline. An alkaline reaction may be due to the presence of hydroxides of the alkalies or alkaline earths, peroxides, carbonates, borates, cyanides, silicates, sulfides (zincates, aluminates, molybdates, tungstates) of the alkalies, as well as ammonia or alkali hypochlorites, etc.

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* Otherwise insoluble basic salts are likely to be formed. If this be the case, as is often shown by the dark color of the residue, add a little concentrated HNO_3, heat the liquid somewhat, and then dilute with water.

If the solution, for example, contains hydroxides or carbonates of the alkalies, it is evident that substances which are precipitated by them cannot be present at the same time, except, in some cases, in the form of complex ions (cyanides, tartrates, etc.)

At once test the solution for peroxides, hydroxides, and carbonates, as well as for the sulfides of the alkalies.

To test for peroxides* (H_2O_2) heat a little of the solution with a few drops of cobalt nitrate solution; a black precipitate shows the presence of H_2O_2.† Or test the solution by adding some titanium sulfate solution and acidifying carefully with cold dilute sulfuric acid; a yellow coloration shows the presence of H_2O_2.‡

A still more sensitive reagent, according to Schöne,§ is a very dilute solution of $FeCl_3 + K_3[Fe(CN)_6]$. If the slightest trace of H_2O_2 is present in the solution, the red solution becomes greenish, and after a time Prussian blue separates out.

In order to detect the presence of hydroxides and carbonates in the presence of H_2O_2, boil a portion of the solution for a long time in a porcelain dish in order to destroy the peroxide, and then add barium chloride until no more precipitate is formed. If the solution now shows an alkaline reaction, the presence of hydroxides‖ is assured. If the precipitate produced by barium chloride dissolves in acid with effervescence, and the gas evolved renders barium hydroxide solution turbid, carbonates are present. If the solution smells of ammonia, evaporate a small portion to dryness in order to see whether other compounds are present, and examine the residue according to A, page 453.

(*c*) The solution reacts acid; it can then contain substances which are soluble in water and in acids, as well as free acids. Evaporate a small portion to dryness in order to see whether any non-volatile matter is present. If no residue is obtained, neutralize the solution with soda and test for acids. If a residue is obtained, examine it according to A, page 453.

D. The Substance to be Analyzed is a Gas

This case is discussed in Vol. II under Gas Analysis.

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* See page 458.

† If the alkaline solution contains hypochlorites or sulfides, these will also give a black precipitate with cobalt nitrate; the above reaction serves only to detect H_2O_2 in the absence of hypochlorites or sulfides. If these last substances are present H_2O_2 is absent, because hypochlorites are reduced to chlorides and sulfides oxidized to sulfates by H_2O_2.

The presence of hypochlorites is usually detected by the odor; on acidifying with dilute H_2SO_4, the odor of chlorine can be detected. Sulfides give off H_2S on being acidified. Hypochlorites and sulfides cannot exist together in the same solution.

‡ H_2O_2 can also be detected by the chromic acid reaction, but this test is less certain than that with titanium sulfate.

§ *Ber.*, **7**, 1695.

‖ Either as such in the original solution or by hydrolysis of peroxides. This test for OH^- ions in the presence of carbonates has been used for years. It is reliable, though care must be taken to add an excess of $BaCl_2$, as otherwise an alkaline reaction may be due to $BaCO_3$, which is more soluble in water than in $BaCl_2$ solution.

TABLE XXI

A. The alloy after being evaporated with nitric acid dissolves in water, forming a clear solution. The alloy contains neither *tin* nor *antimony*. *Add 2 ml of concentrated H_2SO_4 and evaporate until white fumes of sulfuric acid come off thickly.*

RESIDUE. — **SOLUTION.**

White $PbSO_4$.

Wash the precipitate with water and confirm the presence of lead by dissolving in hot NH_4OAc solution and adding K_2CrO_4.

Can contain Bi, Cu, Cd, Fe, Mn, Ni, Co, Zn, Al, P_2O_5.
Saturate with H_2S and filter.

PRECIPITATE. — **SOLUTION.**

Bi_2S_3, CdS, CuS.
Dissolve in hot, dilute HNO_3, filter off the deposited sulfur, add an excess of NH_3 and filter.

PRECIPITATE. — **SOLUTION.**

$Bi(OH)_3$, white. *Dissolve in a little HCl and treat with an alkaline solution of $SnCl_2$.* A black precipitate shows *Bi* to be present.

$[Cu(NH_3)_4]SO_4$
$[Cd(NH_3)_6]SO_4$.
A blue-colored solution shows *Cu*. *Decolorize the solution by the addition of KCN, and add $(NH_4)_2S$.* A yellow precipitate of CdS shows the presence of *Cd*.

$FeSO_4$, $MnSO_4$, $NiSO_4$, $CoSO_4$, $ZnSO_4$, $Al_2(SO_4)_3$, H_3PO_4.
Expel the excess of H_2S by boiling, add a few drops of concentrated HNO_3 to oxidize the iron, then 10 ml of NH_4Cl solution, and NH_4OH drop by drop until the boiling liquid smells of NH_3 permanently; filter the solution quickly.

PRECIPITATE. — **SOLUTION.**

$[Fe(OH)_3$, $Al(OH)_3$, $(AlFe)PO_4]$.
Dissolve in a little HNO_3, and test a little of the solution for Fe by the addition $K_4Fe(CN)_6$. The formation of Prussian blue shows presence of *Fe*.
Test another portion of the solution with considerable ammonium molybdate solution. A yellow crystalline precipitate shows the presence of *P*.
Treat the principal part of the solution with an excess of KOH and filter. Make the filtrate, which may contain any Al as $KAlO_2$, acid with HCl, and treat with NH_4OH. A white, gelatinous precipitate shows the presence of *Al*.

SOLUTION.

$MnCl_2$, $[Co(NH_3)_6]Cl_2$,
$[Ni(NH_3)_6]Cl_2$, $[Zn(NH_3)_6]Cl_2$.
Saturate with H_2S and filter. Reject the filtrate. Treat the precipitate, consisting of sulfides of Mn, Co, Ni, and Zn, with cold dilute HCl and filter.*

RESIDUE. — **SOLUTION.**

NiS, CoS. *Examine according to Table V, p.* 251.

$MnCl_2$, $ZnCl_2$.
Boil off the H_2S, treat the solution with an excess of KOH and filter.

RESIDUE. — **SOLUTION.**

$Mn(OH)_2$. *Fuse a small portion with sodium carbonate and potassium nitrate on platinum foil.* A green melt shows the presence of *Mn*.

K_2ZnO_2. *Add acetic acid and conduct H_2S into the solution.* A white precipitate of ZnS shows *Zn* to be present.

* If neither iron nor aluminum was present in the alloy, test this filtrate for phosphoric acid. Evaporate to a small volume, filter from deposited sulfur if necessary, and test with ammonium molybdate. If the alloy contains magnesium it will be present in this filtrate and must be tested for according to page 273, § 8.

TABLE XXII

B. The alloy, after being evaporated with nitric acid, does not all dissolve in water. The alloy contains tin or antimony, or both.* *Filter.*

RESIDUE.			SOLUTION.
SnO_2, Sb_2O_5, (Sb_2O_4), P_2O_5, As_2O_5, Bi_2O_3, and traces of Cu, Pb, Fe, etc. *Wash with water, add KOH to alkaline reaction, and then 5 to 10 ml of K_2S solution. Heat for some time on the water-bath and filter. [In many cases it is more advantageous to accomplish a similar reaction by fusing with Na_2CO_3, and S in a covered porcelain crucible* (cf. p. 173).]			*Examined according to Table XXI.*
RESIDUE.	SOLUTION.		
Bi_2S_3, PbS, CuS, etc. *Dissolve in HNO_3, filter off sulfur, and add the filtrate to the original solution of the alloy in nitric acid.*	K_2SnS_3, K_3SbS_3, K_3AsS_4, K_3PO_4: *Dilute with water, acidify with dilute HCl, and filter.*		
	PRECIPITATE.	SOLUTION.	
	SnS_2, Sb_2S_3, or Sb_2S_5, As_2S_5. *Dissolve in concentrated HCl, boil, dilute with a little water, filter off sulfur, and test according to Table IV, p. 183, for Sn and Sb.*	KH_2PO_4, KCl. *Evaporate the solution to a small volume, add an excess of NH_4OH and treat with magnesium chloride. A white crystalline precipitate shows H_3PO_4 or P to be present.*†	

* In the case of many alloys containing silicon (iron and steel), silicic acid separates out on the addition of HNO_3. This is usually present in a very small amount, and is detected as described under silicic acid.

† This is confirmed by dissolving the precipitate in HNO_3 and testing with ammonium molybdate solution.

SUPPLEMENT TO PART IV

SEMI-MICRO ANALYSIS

It was recommended on page 452 to take a sample of about 1 g for the systematic detection of the cations present in a solid. For every cation, tests are known which are capable of detecting much less than 1 mg, and, when the chief interest is to establish the identity of a fairly pure substance, a very little sample suffices. In practice work, for example, a student may be given a sample which the instructor knows is barite, $BaSO_4$. He expects the student to identify the sample as $BaSO_4$ and does not know whether 0.02 per cent of $SrSO_4$ is present. If the student reports "a trace of $SrSO_4$ is present" the instructor rarely knows whether this represents especially good work on the part of the student or careless work in attempting to carry out the routine procedure. If, on the other hand, one desires to know whether 0.02 per cent of $SrSO_4$ is present in a sample of barite, he will usually take a sample of more than 1 g and carry out the test in a somewhat different way from that given in the conventional precedure.

In the recent development of chemical analysis, more and more emphasis is placed upon the detection and identification of very small quantities of material. Thus the physician may desire to know whether lead or arsenic is present in the blood stream or in other fluids of the body, and often but little material can be spared for the test. The result has been the development of numerous microchemical tests, many of which have been already described in this book. Many teachers feel that it is best to encourage the student to work with small samples and that all that is necessary for a student to know about qualitative analysis can be taught best by a course in "Semi-micro Qualitative Analysis." The chief objection to this idea is partly that additional equipment is necessary but mainly that the student is required to use numerous organic reagents concerning which he knows but little. The tests become almost a matter of *Magic*. Many students, however, rather like this spirit of mysticism and prefer it to being forced to understand chemical reactions and to being obliged to balance a lot of chemical equations.

In semi-micro qualitative analysis, the weight of sample and the volumes of solutions used are smaller than in ordinary work. About 20 mg of material is taken for the complete detection of cations, and the total volume of solution is usually less than 5 ml, because most of the tests are made with *drops* of solution and drops of reagent. Filtrations are usually avoided, the same result being obtained by the use of a hand centrifuge such as can be purchased for about ten dollars. The solution and precipitate are placed in a 3-ml centrifuge tube, and, after centrifuging, the supernatant liquid (centrifugate) is removed by means of a capillary pipet, or a medicine dropper. To wash the residual precipitate, a little wash liquid is added and mixed with the precipitate by means of a platinum wire, the liquid is centrifuged again, and the supernatant liquid removed as before. If filtration is required, a filter of 25-mm diameter at the top is sufficiently large, and a heavy glass suction flask of not greater than 25-ml capacity is suitable if suction is needed. Test tubes and crucibles of about 5-ml capacity are used, and heating is accomplished with a *micro burner*.

In the following procedure,* the systematic analysis is carried out in much the same way as has been described for *macro* work, except with respect to details in manipulation. To save space, many of the *Chemical Abstracts* abbreviations are used in the description (cf. p. 93).

Most of the tests described on pages 453–460 require very little material. The charcoal and bead tests, however, can be omitted if the worker has not already had considerable experience with blowpipe analysis. The closed-tube test and the test with concentrated sulfuric acid should always be tried; in the last test use a 2-ml test tube or a 5-ml crucible (cf. pp. 453, 458).

Test for NH_4^+. — To about 2 mg of the sample, or the residue obtained by evaporating a few drops of a soln. to dryness, add a few drops of 3 *N* NaOH, heat gently, and test the escaping vapors with moist, red litmus paper. Note also whether there is any perceptible odor (cf. p. 290).

Tests of Solubility. — To a very small portion of the sample in a 5-ml test tube (or a smaller one) add a few drops of water and heat over a small flame. Note whether water has any appreciable solvent effect, and, if it has, test the soln. with litmus. If water does not dissolve the sample, test the same way with HCl, HNO_3, aqua regia, etc. The procedure is like that described on pages 460–467 except that these expts. are carried out in a very small test tube and with only a few mg of sample.

SYSTEMATIC CATION ANALYSIS

The systematic procedure follows the same plan as that outlined in Table VIII on page 471. The sample taken for analysis should weigh about 20–50 mg, and it should be prepared, as indicated by the preliminary tests of soly., with about 2 ml of solvent. If HCl is used for dissolving or decomposing the sample, Ag, mercurous Hg, and possibly Pb will ppt. as chlorides upon dilution and the residue must be examined for Ag, Pb, Hg, and other insoluble substances (cf. pp. 466–471).

Group I

Precipitation. — Place 1 ml of an aq. or dil. HNO_3 soln. in a 3-ml centrifuge tube, add 1 drop of concd. HCl (or more if necessary), and stir with a Pt wire. Take out the wire and touch the end of it to a piece of blue litmus paper, to make sure that the solution is acid. A turbidity which clears on the addition of a little more acid indicates the presence of Bi, Sb, or Sn; it must be remembered, however, that AgCl dissolves in an excess of strong HCl, and ppts. on diluting. If no ppt. forms, pass on to Group II.

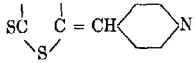
If a ppt. of insoluble chlorides is formed, heat the soln. to boiling, place in the cen-

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* Cf. G. Gutzeit, *Helv. Chim. Acta*, **12**, 829 (1929); Heller and Krumholz, *Mikrochemie*, **7**, 213 (1929); F. Feigl, *Tüpfelreaktionen*, 2nd ed. (1935); K. Heller, *Mikrochemie*, **8**, 33 (1930); C. J. van Nieuwenburg, *Mikrochemie*, **8**, 199 (1931); van Nieuwenburg and Dulfer, *Qualitative Analysis by Drop Tests*, 2nd ed. (1935); Engelder, Dunkelberger, and Schiller, *Semi-micro Qualitative Analysis* (1936); Behrens and Kley, *Mikrochemische Analyse* (1921); Benedetti-Pichler and Spikes, *Introduction to Microtechnique of Qualitative Analysis* (1935); Emich-Schneider, *Microchemical Laboratory Manual* (1935); Winkley, Yanowski, and Hynes, *Mikrochemie*, **21**, 102 (1936).

trifuge, balance with a similar tube, and rotate both tubes to throw the ppt. into the bottom of the tube. Pour off the centrifugate, or remove it by means of a capillary pipet or a medicine dropper. Add 2 ml of hot water, again centrifuge, and add this centrifugate (which may contain $PbCl_2$) to that first obtained. Repeat this treatment with hot water at least once more but discard the centrifugates after two treatments with hot water. Test the first centrifugate with a drop of HCl to make sure that enough was added to cause complete pptn. If more ppt. forms, treat it again as just described, but pay no attention to a crystalline ppt. of $PbCl_2$ which may form on cooling but is easily distinguished from the curdy ppts. of AgCl and Hg_2Cl_2 (cf. p. 115).

Detection of Ag and Hg. — To the ppt. in the centrifuge tube, add 5 drops of 5 per cent KCN soln., heat gently over a micro burner, and centrifuge. The resulting soln. will contain $Ag(CN)_2^-$ or $Hg(CN)_2^-$ if Ag or mercurous Hg is present. Place 1 drop of this soln. on spot test paper,* add 1 drop of 2 *N* HNO_3, and follow this with a drop of a satd. soln. of *p*-dimethylaminobenzilidinerhodanine,



in acetone. If Ag is present a red stain will form.

Mercuric ions give a similar test in the absence of cyanide (cf. p. 121).

Place another drop of the soln. upon spot test paper, and at the same place on the paper add 1 drop of freshly prepared $SnCl_2$ soln. and a drop of clear, freshly distd. aniline. A black, brown, or gray spot (due to finely divided Hg) shows that Hg_2^{++} was present in the original sample (cf. p. 107).

Group II

Precipitation. — Take the centrifugate from Group I, or the original solution if no precipitate of AgCl or Hg_2Cl_2 was formed, and evaporate, if necessary, to about 1 ml. Add 1 ml of concd. HCl and heat to boiling. Saturate with H_2S under pressure for five minutes. Reduce the acidity to about 0.3 *N* by adding concd. NH_4OH from a capillary pipet, boil again, and introduce H_2S for three minutes more. Centrifuge, remove the centrifugate, and wash the ppt. with 3 ml of hot water. Centrifuge again, and add this second centrifugate to the first one. Again sat. with H_2S to make sure that pptn. of Group II is complete. If the pptn. was incomplete, transfer the centrifugate in which the new ppt. is suspended to the centrifuge tube contg. the original sulfide ppt. and again centrifuge. Wash the ppt. with hot, 1 per cent NH_4Cl soln. and then with 1 per cent NH_4NO_3 until the soln. shows only a slight acidity. Add the first two washings to the centrifugate containing Groups III, IV, and V (cf. p. 180).

Separation into Subgroups. — To the residue in the centrifuge tube add 5–10 drops of Na_2S reagent (p. 91), stir with a Pt wire, and heat for at least 1 min. Centrifuge and transfer the centrifugate to another centrifuge tube. It will contain AsS_4^{---}, SbS_4^{---}, SnS_3^{--}, and HgS_2^{--} if these elements are present, and the residue may contain PbS, Bi_2S_3, CuS, and CdS (cf. p. 180).

To the residue add 3 more drops of reagent, a little water, stir, heat, and centrifuge again. Repeat these operations until the extraction of the Hg, As, Sb, and

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* A suitable paper is C. S. & S. 601. The paper is called *Tüpfelpapier* and is used for *Tüpfelreaktionen* (spot tests). It is sometimes called "drop reaction paper."

Sn is complete. Test each centrifugate by taking a drop on a glass slide and adding a slight excess of HCl. Compare the result with that obtained by treating a drop of the reagent similarly: if As, Sb, Sn, or Hg is present a precipitate of HgS, As_2S_5, Sb_2S_5, or SnS_2 will be obtained (cf. p. 180).

Analysis of the Copper Group. — Wash the undissolved sulfide with portions of hot water, centrifuge and remove the centrifugate each time, until the washings are only slightly basic to litmus. Add to the washed residue 5 drops of 3 *N* HNO_3 and boil carefully for a min. Centrifuge and transfer the soln. to a small crucible. Repeat this treatment with small portions of HNO_3 until all the Pb, Bi, Cu, and Cd is in soln. The residue is usually S enclosing a little unattacked sulfide. It sometimes contains HgS. It can be tested for Hg by dissolving in HCl and $KClO_3$ and testing with $SnCl_2$ as described for the examn. of the As-Sn subgroup.

To the soln. in the crucible, add 3 drops of concd. H_2SO_4 and evap. carefully until dense fumes of H_2SO_4 are evolved. Cool and transfer, with a pipet, to a centrifuge tube containing 3–5 drops of cold water. Centrifuge, and use the centrifugate for the Bi, Cu, and Cd tests.

Detection of Pb. — Wash the $PbSO_4$ residue with two 2-ml portions of water, using the centrifuge each time and adding the centrifugate to the main soln. To the washed residue add 3 drops of 3 *N* $NH_4C_2H_3O_2$ soln., and heat to dissolve the $PbSO_4$. To the resulting soln. add 1 drop of K_2CrO_4 reagent. A yellow ppt. of $PbCrO_4$ shows that Pb is present (cf. p. 112).

Detection of Bi. — To the soln. obtained from the $PbSO_4$ test, add strong NH_4OH from a pipet until the soln. is basic. This serves to ppt. $Bi(OH)_3$ and leaves Cu and Cd in soln. as ammoniates. If ppt. forms, remove and wash it with the aid of the centrifuge. Test the residue for Bi by the Na_2SnO_2 reaction (cf. p. 125). It is convenient to transfer a little of the $Bi(OH)_3$ ppt. to a piece of filter paper and moisten the paper with a drop of freshly prepared Na_2SnO_2 soln.

Detection of Cu. — If the soln. has a blue color no further test is necessary. If in doubt, transfer a drop of the soln. to a white spot plate, make acid with $HC_2H_3O_2$, and add a drop of $K_4Fe(CN)_6$ reagent. A red ppt. of $Cu_2Fe(CN)_6$ proves the presence of Cu (cf. p. 137).

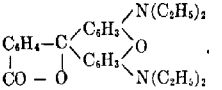
Detection of Cd. — If Cu is present, add to the soln. 5 drops of *N* KCN soln. or sufficient to accomplish complete decolorization of the blue soln., and sat. with H_2S. A yellow ppt. of CdS shows the presence of Cd. If Cu is absent, merely make the ammoniacal soln. slightly acid with H_2SO_4 and introduce H_2S.

Analysis of the Tin Group. — Make the centrifugate from the Na_2S treatment just acid with 3 *N* HCl to ppt. the sulfides of Hg, As, Sb, and Sn. Centrifuge, and discard the centrifugate. To the residue add about 5 drops of concd. HCl and boil to dissolve Sb_2S_5 and SnS_2. Dilute with 5 drops of water, centrifuge, and transfer the centrifugate to a small test tube. Wash the residue several times with 1-ml portions of hot water. Add the first washing to the $SbCl_5$-$SnCl_4$ solution but discard the rest. To the residue in the centrifuge tube, add 3–6 drops of 6 *N* NH_4OH. Stir, heat, and transfer the supernatant liquid to another centrifuge. Wash thoroughly with 6-drop portions of NH_4OH, and add each washing to the ammoniacal soln. that may contain AsO_4^{---} and AsS_4^{---}. Test each portion by taking a drop of the ammonia extract, adding acid, and seeing if any yellow As_2S_5 ppt. is formed. Treat with NH_4 water until the last centrifugate fails to give a yellow ppt. on adding acid.

Detection of Hg. — If a black residue remains after the ammonia treatment it is probably HgS. Dissolve in a little concd. HCl and a crystal of $KClO_3$, transfer to a small crucible, and test for Hg as described under the analysis of Subgroup As-Sn.

Detection of As. — Add HCl to a portion of the ammoniacal soln. until the reaction is acidic. A yellow ppt. at this point is indication that As is present (cf. p. 144). To the remainder of the ammoniacal soln. in a small tube, add a little Zn and a few drops of 6 *N* H_2SO_4. Make sure that an excess of acid has been added, by testing a drop of the soln. with litmus, insert a plug of cotton wet with $Pb(C_2H_3O_2)_2$ soln., and over the tube place a strip of paper moistened with 50 per cent $AgNO_3$ soln. (cf. p. 155). A yellow or gray spot is $AsAg_3 \cdot AgNO_3$.

Detection of Sb. — To 1–2 drops of the $SbCl_5$-$SnCl_4$ solution on a spot plate, add some small crystals of $NaNO_2$ and 1–2 drops of concd. HCl. When effervescence has stopped, add a drop of 0.01 per cent aqueous soln. of the dyestuff rhodamine B,



. If Sb is present the bright red, fluorescing soln. of the dye will assume a violet tint. Place another drop of the soln. on a glass slide, heat nearly to boiling, and add a crystal of $Na_2S_2O_3 \cdot 5\ H_2O$; a red color of antimony oxysulfide is shown on the surface of the crystals if Sb is present (cf. p. 162).

Detection of Sn. — Prepare some phosphomolybdic acid by treating a soln. of alkali phosphate with HNO_3 and an excess of ammonium molybdate reagent. Dissolve some of the yellow ppt. in hot aqua regia, evap. the soln. to dryness, dissolve the residue in water, and purify the phosphomolybdic acid by recrystallization from water. Impregnate some filter paper with a little of the aqueous soln. and hold over the fumes of NH_3. Reduce the HCl centrifugate contg. $SbCl_3$ and $SnCl_4$ with a strip of Mg ribbon. Filter and place 1 drop of the reduced soln. upon the paper which was impregnated with phosphomolybdic acid; if $SnCl_2$ is present, a dark blue stain forms immediately. The test can be obtained with 0.03 γ of Sn. Sb^{+++} gives a similar test if the paper is held in steam, but the above treatment with Mg (or Zn) reduces $SnCl_4$ to $SnCl_2$ (which is necessary) and precipitates Sb, which does not interfere.

Group III

If H_3PO_4, $H_2C_2O_4$, or HF is present in the centrifugate from Group II, the analysis is complicated (cf. p. 250) by the fact that Ca, Sr, Ba, and Mg may ppt. with Group III. The presence of Cr also causes trouble (cf. p. 198). A method of analysis in the absence of phosphate will be given based on the assumption that Fe, Al, and Cr can be separated from Ni, Co, Mn, and Zn by means of NH_4OH. Then it will be shown how the analysis can be conducted when the above interfering substances are present.

Absence of Oxalate, Tartrate, Fluoride, and Phosphate

Place the soln. from which Group II has been removed by means of H_2S in a 5-ml centrifuge tube, add 5 drops of Br_2 water to oxidize Fe^{++}, and boil off excess Br_2. Add 5 drops of 10 per cent NH_4Cl to prevent pptn. of $Mg(OH)_2$, and make distinctly alk. with concd. NH_4OH. Stir with a Pt wire, and centrifuge. Transfer the centrifugate to another tube, wash twice with 1-ml portions of 6 *N* NH_4OH, and add the washings to the main centrifugate, which may contain $Ni(NH_3)_4^{++}$, $Co(NH_3)_4^{++}$, $Zn(NH_3)_4^{++}$, and Mn^{++} besides alk. earths and alkalies (Division B). The residue may contain $Fe(OH)_3$, $MnO(OH)_2$, $Cr(OH)_3$, and $Al(OH)_3$ (Division A).

Division A

Separation of Fe and Mn from Cr and Al. — To the residue, add 3 drops of water, 3 drops of 6 *N* NaOH, and small portions of Na_2O_2 powder while keeping the soln. cool. When effervescence stops, centrifuge, and transfer the centrifugate to another tube. The residue may contain $Fe(OH)_3$ and $MnO(OH)_2$ (1). The centrifugate may contain AlO_2^- and CrO_4^{--} (2). Wash the residue with small portions of cold water. Dissolve the residue in 4 drops of dilute HNO_3 and a few drops of 3 per cent H_2O_2.

(1) *Detection of Fe.* — Place a drop of the soln. on a white spot plate; add 1 drop of dil. HCl and 1 drop of $K_4Fe(CN)_6$ reagent (cf. p. 215).

If the test is positive, it is desirable to know whether Fe^{++}, Fe^{+++}, or both are present in the original sample. Digest a few mg of the sample with concd. HCl, evap. off most of the excess acid, and dil. with a few drops of water. Into each of 3 depressions on a white spot plate, place 1 drop of the soln. and test separately with 1 drop of KCNS reagent, 1 drop of $K_4Fe(CN)_6$ reagent, and 1 drop of a freshly prepared soln. of about 5 mg of $K_3Fe(CN)_6$ in 5 ml of water (cf. pp. 211, 215).

Detection of Mn. — To 1 drop of the soln. on the spot plate add a slight excess of powdered $NaBiO_3$ (cf. p. 226).

(2) *Detection of Cr.* — Unless the soln. is yellow, no test should be made. To 1 drop of the acid soln. on a spot plate add $HC_2H_3O_2$ and a little powdered $Pb(C_2H_3O_2)_2$. A yellow precipitate indicates Cr (cf. p. 204). To a drop of the soln. in a small test tube add 1 drop of concd. HNO_3 and several drops of 3 per cent H_2O_2. Mix, add an equal vol. of ether, and look for a blue color in the ether layer (cf. p. 202).

Detection of Al. — Make the rest of the AlO_2^- and CrO_4^{--} soln. barely acid with HNO_3, add some solid $NH_4C_2H_3O_2$, 5 drops of either alizarin, alizarin S, or aluminon reagent, and NH_4OH to a basic reaction. Centrifuge, and look for a red color on the $Al(OH)_3$ precipitate (cf. p. 191).

Division B

Take the filtrate from the sepn. of Division A from Division B and sat. it with H_2S to ppt. NiS, CoS, MnS, and ZnS. If a ppt. forms, centrifuge, and save the centrifugate for the Group IV and V tests. Wash the ppt. with small portions of hot water, and add the washings to the first centrifugate. Dissolve the ppt. in 1 ml of 6 *N* HCl, adding a little $KClO_3$ if necessary. Evaporate off Cl_2 and about half of the acid.

Detection of Ni. — Transfer 1 drop of the soln. to a spot plate; add 1 drop of dimethylglyoxime reagent and 1 drop of 6 *N* NH_4OH (cf. p. 233, § 10).

Detection of Co. — To 1 drop of the soln. on the spot plate add just enough NH_4OH to leave the solution slightly acid, add 1 drop of a reagent prepared by dissolving 0.1 g of α-nitroso-β-naphthol in 20 ml of water to which 1 ml of 6 *N* NaOH has been added, filtering and diluting to 200 ml. Look for a reddish brown precipitate (cf. p. 242, § 14).

Detection of Mn. — Evap. 1 drop of the soln. with HNO_3 and test as above with $NaBiO_3$.

Detection of Zn. — Prepare some cobalticyanide test paper by dissolving 4 g of $K_3Co(CN)_6$ and 1 g of KCl in 100 ml of water, moisten a piece of filter paper with this soln., and dry at room temp. or at 100°. To the remainder of the soln. which has been tested for Ni, Co, and Mn, add HNO_3 until about 5 per cent of acid is present (1 ml of concentrated HNO_3 contains approximately 1 g of HNO_3). Transfer a drop

of this soln. to a disk of the test paper, of about 1-cm diameter. Dry over a micro burner, and burn the paper. If Zn is present, the ash will show a green color (cf. p. 250).

Presence of Tartrate, Oxalate, Fluoride, or Phosphate

A. Presence of Oxalate, Tartrate, or Fluoride. — Evaporate the filtrate from Group II to dryness in a porcelain crucible. Add a few drops of concd. H_2SO_4 and heat until fumes of H_2SO_4 are evolved. If charring results, cool, add a few drops of concd. HNO_3, and heat until dense fumes of H_2SO_4 are again evolved. Repeat this treatment until the soln. is practically clear. Cool, dil. with water, add 3 times as much alcohol, and centrifuge. The residue may contain $BaSO_4$, $SrSO_4$, and $CaSO_4$. The centrifugate may contain Group III, Mg and the alkalies. Wash the residue with small portions of 6 *N* H_2SO_4 which has been diluted with 3 times as much alcohol. Transfer the residue to a porcelain dish, add 2 ml of 3 *N* Na_2CO_3, cover the dish with a watch glass, and heat on the water bath. Transfer to a centrifuge tube, with the aid of hot water. Centrifuge the mixture and discard the centrifugate. Repeat this treatment with Na_2CO_3 twice more, and discard the centrifugate each time. In this way, the sulfates of Ba, Sr, and Ca are changed, for the most part, to insol. carbonates (cf. p. 268). Dissolve in a few drops of 6 *N* HNO_3, and test for Ba, Sr, and Ca as will be described for the analysis of Group IV.

B. Presence of Phosphate. — The above treatment with H_2SO_4 also overcomes much of the trouble caused by phosphates in the analysis of Group III. The following procedure serves to remove phosphate ions (cf. p. 250).

Boil the centrifugate from Group II to remove H_2S and then add sufficient H_2O_2 to oxidize the Fe^{++}. Make barely ammoniacal with NH_4OH, and dissolve the ppt. by dropwise addn. of HCl, avoiding an excess (if no ppt. forms on adding ammonia, no member of Groups III and IV can be present except Ni, Co, and Zn whose phosphates are easily dissolved by excess NH_3). Test a portion of the soln. for Fe^{+++}, as described above. To the slightly acid soln. add 0.25 g of solid $NH_4C_2H_3O_2$ (cf. pp. 190, 213). If more than sufficient Fe^{+++} is present to form $FePO_4$ with all the PO_4^{---} present, the soln. will turn red. If not, add $FeCl_3$ soln. until it does. Add a little water, and heat to boiling. The precipitate may contain $FePO_4$, $Fe(OH)_2 \cdot C_2H_3O_2$, $AlPO_4$, and $CrPO_4$. Examine the precipitate for Al and Cr, and test the centrifugate for Mn, Ni, Co, Zn, Ca, Br, Mg, K, and Na according to the regular procedure.

Group IV

To the centrifugate from Group III add a little solid NH_4Cl and $(NH_4)_2CO_3$ reagent sufficient to ppt. all Ba, Sr, and Ca as carbonates (cf. p. 275). Centrifuge, and reserve the centrifugate for the Group V tests.

Detection of Ca. — Dissolve the carbonate ppt. in as little HNO_3 as possible. Transfer the soln. to a small porcelain dish, and evaporate to dryness. Heat the dry residue with the free flame, moved about the bottom of the dish, to make sure that it is anhydrous. Crush the dried and cooled residue and add about 1 ml of *absolute* acetone. Stir and pipet off the supernatant liquid, which may contain $Ca(NO_3)_2$. Save the residue for the Ba and Sr tests. To the acetone solution, add a drop of $(NH_4)_2C_2O_4$ reagent and 5 drops of water. If a white ppt. forms it is probably CaC_2O_4. Test in the flame after moistening with HCl (cf. p. 264).

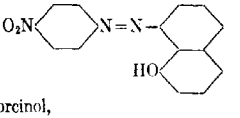
Detection of Ba. — Dissolve the residue, insoluble in acetone, in a little water; add 2 drops of 6 *N* $HC_2H_3O_2$ and an equal vol. of 3 *N* $NH_4C_2H_3O_2$ solution. Heat,

and to the boiling soln. add dropwise sufficient K_2CrO_4 to precipitate all the Ba. Centrifuge the mixture, and save the centrifugate for the Sr test. Dissolve the residue in dil. HCl (avoid an excess), test in the flame and, in case of doubt, dil. with twice as much water and test with a drop of dil. H_2SO_4.

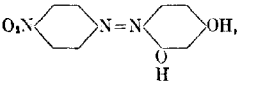
Detection of Sr. — To the centrifugate from the $BaCrO_4$ ppt. add NH_4OH dropwise until the liquid is lemon colored; a pale yellow precipitate is $SrCrO_4$ (cf. p. 265, § 6). Confirm by the flame test.

Group V

Detection of Mg. — To 1 drop of the centrifugate from Group IV, add 1–2 drops of a soln. made by dissolving 1 mg of *p*-nitrobenzene-azo-α-naphthol,



or *p*-nitrobenzene-azo-resorcinol,



in 2 *N* NaOH. A blue color shows the presence of Mg. Care must be taken to make sure that the soln. is basic. If the soln. tested is strongly acid, a few drops of NaOH soln. should be added. The test is exceedingly delicate and will show the presence of Mg in tap water or in the ash of a qualitative filter paper. If, therefore, a very pale test is obtained, a blank test should be made with a drop of the distilled water.

Detection of NH_4. — This test is always made on the original sample and has been described (p. 290, § 1 or 292, § 8).

Removal of NH_4 Salts. — To the remainder of the soln. after the Mg test, add an excess of HNO_3 and evaporate to dryness in a small porcelain dish. Heat the residue over a free flame by holding the burner in the hand and keeping the flame moving slowly over the entire outside of the dish. Continue heating until no more fumes are evolved. Cool, wash down the sides of the dish with a little water, and repeat the evaporation and heating. Finally digest the residue with 1 ml of hot water and filter.

Detection of K. — Place a drop of the soln. on the spot plate, add a drop of $AgNO_3$ reagent and a little solid $Na_3Co(NO_2)_6$. A yellow ppt. denotes K (cf. p. 282). Test in the flame, and view through blue glass.

Detection of Na. — Add 16 drops of $Mg(C_2H_3O_2)_2 + UO_2(C_2H_3O_2)_2$ reagent to 2 drops of the soln. in a small test tube. A pale yellow ppt. which forms slowly indicates Na (cf. p. 285).

Detection of Li. — To the rest of the soln. add a drop of concd. NH_4OH and one-tenth of the soln.'s vol. of 0.2 *N* Na_2HPO_4. A white ppt. indicates Li (cf. p. 598). The ppt. should give a red flame coloration when moistened with HCl and touched with a platinum wire, which is then held in the non-luminous flame.

SYSTEMATIC ANION ANALYSIS

The preliminary examn. for acidic constituents should be carried out as described on pages 458–460, but with little substance. The methods of preparing a soln. for the analysis are the same as those discussed on pages 474–478. For microchemical work it is convenient to divide the anions into 3 groups.* In most cases, the "prepared soln." is obtained by boiling the sample with Na_2CO_3, and filtering.

Group I

Carbonate, Cyanide, Nitrite, Sulfide, Sulfite, and Thiosulfate

Preliminary Test. — Place about 10 mg of the sample in a 5-ml test tube, add a little water, heat to boiling, and add a few drops of dil. HCl. Effervescence may be caused by escape of CO_2 (colorless and odorless gas) from a carbonate, SO_2 (gas with the odor of burning sulfur) from a sulfite or thiosulfate, H_2S (odor of rotten eggs) from a decomposable sulfide, HCN (odor of bitter almonds) from a cyanide, and NO_2 (brown fumes) from a nitrite. Sulfur may be deposited from a thiosulfate or from the action of H_2S and SO_2.

Detection of CO_3^{--}. — See pages 372 and 479.

Detection of CN^-. — As a rule the odor suffices to detect the poisonous HCN which is liberated by the action of acid on a simple cyanide. To detect CN^- in an aq. soln. of an alkali cyanide, place 1 drop of the soln. in a small porcelain crucible, add 1 drop of 3 *N* H_2SO_4, and cover the crucible with a filter paper which has been impregnated with copper-benzidine acetate. The paper will turn blue when escaping HCN reacts with it. Oxidizing and reducing substances must be absent.

To prepare the test paper, mix, shortly before using, a little of a soln. of 2.86 g $Cu(C_2H_3O_2)_2 \cdot H_2O$ per liter of water with an equal vol. of a soln. prepared by diluting 475 ml of satd. aq. benzidine acetate solution with 525 ml of water. In the test, a blue quinoidal oxidation product of benzidine is formed; the test in inconclusive in the presence of oxidizing or reducing substances. The oxidation of the benzidine is due to the reduction of the Cu^{++} to colorless cuprocyanide complex (cf. p. 136).

Detection of NO_2^-. — The appearance of brown fumes on adding dilute HCl is sufficient indication. The gas will liberate iodine and turn iodo-starch paper blue. The test with sulfanilic acid (p. 348) is very sensitive.

Detection of S^{--}. — If H_2S is evolved, the lead acetate test is sensitive (p. 352).

Detection of SO_3^{--}. — The noticeable escape of a gas with the odor of SO_2, when the sample is treated with dil. HCl, serves to detect the presence of sulfite in a small quantity of sample. If HCN, NO_2, and H_2S are absent, the bleaching effect of the gas upon a drop of $KMnO_4$ solution held in the loop of a platinum wire indicates sulfite (cf. also p. 367, § 14, and p. 487).

Detection of $S_2O_3^{--}$. — The following test will show the presence of $S_2O_3^{--}$ even in the presence of S^{--} and depends upon the fact that $HgCl_2$ reacts with H_2S to form white $2\,HgS \cdot HgCl_2$ and with $S_2O_3^{--}$ to form HgS and H_2SO_4. $S^{--} + Hg^{++} \rightarrow \mathbf{HgS}$. $S_2O_3^{--} + Hg^{++} + H_2O \rightarrow \mathbf{HgS} + SO_4^{--} + 2\,H^+$. Place a drop of the neutral soln. upon the spot plate and mix with a drop of 2 per cent $HgCl_2$ soln. Then add a little KCl, to convert excess $HgCl_2$ to $KHgCl_4$, and test with blue litmus paper. If thiosulfate was present it will turn red.

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* Cf. Engelder, Dunkelberger, and Schiller, *Semi-micro Qualitative Analysis*, New York (1936).

Group II

Arsenite, Arsenate, Phosphate, Silicate, Fluoride, Sulfate, Borate, Oxalate, Tartrate, and Chromate

Preliminary Tests. — To a few drops of the prepared soln. (cf. p. 482) add a slight excess of HCl and boil off CO_2. Neutralize carefully (cf. Table X, p. 477) with NH_4OH, till a tiny drop of the solution gives a neutral reaction when placed on litmus paper. Add 1 drop of $BaCl_2$ reagent and 1 drop of $CaCl_2$ reagent (cf. p. 483). If no ppt. forms, the acids of this group are probably absent although it must be remembered that certain phosphates, fluorides, and silicates are not decomposed much by boiling with Na_2CO_3 soln. and borates of Ca or Ba form slowly, if at all, in the presence of NH_4 salt. A yellow ppt. with the group reagent is $BaCrO_4$.

Detection of AsO_3^{---}. — To a few drops of the soln. add 1 drop of 6 *N* HCl (or more if necessary to give an acid reaction) and introduce H_2S. If a yellow ppt. of As_2S_3 forms immediately, AsO_3^{---} is present. Test a fresh portion of the soln. by reactions 4 and 9 on pages 145, 147.

Detection of AsO_4^{---}. — To a few drops of the soln. add a liberal excess of HCl, heat to boiling, and sat. with H_2S. If a yellow precipitate is formed (cf. p. 148) AsO_4^{---} is probably present. Confirm by reaction 7 or 8 on page 150.

Detection of PO_4^{---}. — To a few drops of the soln. add 6 *N* HNO_3 in excess. Heat to boiling and add 1 ml of $(NH_4)_2MoO_4$ solution (cf. p. 400). If arsenic acid is present, carry out the test after first removing arsenic as sulfide with H_2S.

Detection of SiO_3^{--}. — Place a drop of the soln. in a centrifuge tube; add 1 drop of 6 *N* NH_4OH and 3–5 drops of 6 *N* NH_4NO_3 solution. A gelatinous precipitate indicates SiO_3^{--}. Repeat the test, using concentrated HCl instead of NH_4OH. If these two tests are negative, and the substance is insoluble in acids, fuse some of the substance with Na_2CO_3 in a platinum crucible. Leach the cold melt with hot water and then try the above test. If a positive test is obtained, perform the Daniel test (p. 447).

Detection of F^-. — Place a little of the sample in a small *glass* tube, add a few drops of H_2SO_4, heat, and test the escaping vapor with a drop of water (cf. p. 437).

Detection of SO_4^{--}. — Cf. page 433, § 1.

Detection of BO_3^{---}. — Place a few mg of the solid sample (or the residue obtained by making a soln. alk. with NaOH and evaporating to dryness) in a glass test tube; add a little methyl alcohol and a few drops of concd. H_2SO_4. In the mouth of the test tube, place a rubber stopper carrying tubes like those of a wash bottle. In this case, however, draw the end of the short tube out to a capillary and blow through the longer tube which dips into the liquid. Blow the vapors from the soln. into the non-luminous flame of a small burner; if H_3BO_3 is present, vapors of its very volatile methyl ester will impart to the flame a brilliant green color. There is a slight danger of explosion if the exit tube from the test tube is not drawn out to a capillary. Very little H_3BO_3 suffices to give the test. It is never wise to evaporate an aq. acid soln. to dryness before applying the test because H_3BO_3 is volatile with steam.

Detection of $C_2O_4^{--}$. — To a little of the Na_2CO_3 soln. add $HC_2H_3O_2$ to acid reaction and some $CaCl_2$ reagent. If a ppt. forms, it is probably CaC_2O_4 or CaF_2. Centrifuge, wash the ppt. with hot water, and dissolve it in a few drops of hot, 6 *N* H_2SO_4. To the hot soln. add 2 drops of 6 *N* H_2SO_4 and a small drop of $KMnO_4$ soln. Look for decolorization and evolution of CO_2 (p. 380, § 8).

Detection of $C_4H_4O_6^{--}$. — Heat a little of the sample in a crucible with concentrated H_2SO_4. Charring and an empyreumatic odor indicate the presence of a tartrate.

To confirm this indication, take 0.20 g of sample and, if the sample is not the free acid or an alkali salt, boil it with a little 3 *N* K_2CO_3. Centrifuge, and make the soln. acid with glacial $HC_2H_3O_2$. Cool, and stir vigorously, which should cause the formation of $KHC_4H_4O_6$ (cf. p. 385, § 10). If a ppt. forms, decant off the liquid and wash the crystals with 50 per cent alc. Dissolve in a little NH_4OH and add $CaCl_2$ reagent. Filter, and wash with cold water. Digest the ppt. with cold 6 *N* NaOH; boil the NaOH extract to see if a ppt. forms (cf. p. 384, § 5).

Detection of CrO_4^{--}.—Unless the soln. is yellow, CrO_4^{--} is absent. If Cr was found in the tests for cations, it may be present as CrO_4^{--} (or $Cr_2O_7^{--}$). Place 2 drops of the prepared soln. in a small test tube; add a drop of concentrated HNO_3, 3–5 drops of ether, and 1–3 drops of H_2O_2 (cf. p. 202).

Group III

Ferricyanide, Ferrocyanide, Thiocyanate, Iodide, Bromide, and Chloride

To test for the group place a few drops of the prepared soln. in a small test tube, make acid with HNO_3, heat to boiling, and add a drop or two of $AgNO_3$ reagent (cf. Table XVI). $Ag_3Fe(CN)_6$ is reddish brown and sol. in NH_4OH. $Ag_4Fe(CN)_6$, AgCNS, and AgCl are white, and the last two are sol. in NH_4OH. AgI is distinctly yellow and insol. in NH_4OH. AgBr is pale yellow, and its soly. in NH_4OH (as well as in HNO_3) lies between that of AgI and AgCl.

Detection of $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$, CNS^-. — Cf. pp. 334, § 7; 337, § 10; 340, § 7. On spot test paper, place a drop of *N* $Pb(NO_3)_2$ soln. and a drop of the prepared soln. which has been acidified with $HC_2H_3O_2$. $Pb_2Fe(CN)_6$ will be formed at the center of the spot, while CNS^- and $Fe(CN)_6^{---}$ will move farther away from the center. Add a drop of water to the center of the spot to cause further spreading of the last 2 anions. When the spot has ceased spreading, make a narrow line across the spot with a 0.1 *N* soln. of $FeCl_3$ in a capillary pipet. Perpendicular to this line, draw a similar narrow line with a 0.1 *N* soln. of $FeSO_4$. If all 3 anions are present, Prussian blue will be formed near the middle of the spot along the $FeCl_3$ line, a little farther away on the same line red $Fe(CNS)_3$ will appear, and on the outer edge of the $FeSO_4$ line Turnbull's blue will be found.

Detection of I^- *and* Br^-. — Take a little of the prepared soln. in a small test tube, add sufficient CCl_4 to form a distinguishable layer below the aq. soln., and slowly introduce drops of NaOCl soln. After the addn. of each drop, shake and examine the CCl_4 layer. I_2, liberated first (cf. p. 321), colors the CCl_4 reddish violet. Further addn. of NaOCl oxidizes the I_2 to HIO_3 which is colorless; then add a few drops of 6 *N* H_2SO_4 and the yellow color of Br_2 appears in the CCl_4 solution. It is well to carry out a blank test with water if the Br test is doubtful.

Detection of Cl^-. — This is the commonest anion of this group, and usually the formation of a white ppt. in a soln. which is acid with HNO_3 is sufficient evidence of Cl^- but this ppt. is similar in appearance to $Ag_4Fe(CN)_6$, AgCNS and is not much different from AgBr. If another anion of this group is present, take some of the prepared soln., neutralize with HNO_3, and introduce $KMnO_4$ soln. until a faint purple MnO_4^- color persists. Centrifuge, and discard the ppt. Add $Hg(NO_3)_2$ soln., centrifuge, and again discard the ppt. Make acid with HNO_3, add $AgNO_3$, centrifuge, and discard the soln. Dissolve the ppt. in a few drops of concd. NH_4OH and be sure that AgCl forms again on making acid with HNO_3. If a very faint test for Cl^- is obtained, make a blank test with all the reagents used; sodium carbonate almost always contains a trace of chloride and frequently a little chloride gets into the HNO_3 bottle from careless interchange of reagent bottle stoppers.

Group IV

Acetate and Nitrate

Detection of $C_2H_3O_2^-$. — To a few drops of the soln. in a small test tube add 5 drops of ethyl alc. and 5 drops of concd. H_2SO_4. The characteristic odor of ethyl acetate can be recognized if acetate is present (cf. p. 357, § 2).

To another portion add $Ba(NO_3)_2$ to remove interfering ions, filter, and to the filtrate add a drop of 5 per cent $La(NO_3)_3$, a drop of 0.02 *N* iodine in alc., and several drops of dil. NH_4OH. Heat to boiling and look for a blue color (cf. p. 358).

Detection of NO_3^-. — Boil at least 10 mg of the sample with water. Filter, if necessary, and evaporate to a small vol. In a cavity on the spot plate, place a tiny fragment of $FeSO_4 \cdot 7\ H_2O$ (or of Mohr's salt), a drop of the soln. to be tested, and a drop of concd. H_2SO_4. A brown ring will form around the crystal of Fe^{++} salt if nitrate is present (cf. p. 418, § 6).

PART V. REACTIONS OF THE RARER METALS

METALS OF THE H_2S GROUP

MOLYBDENUM, SELENIUM, TELLURIUM, GERMANIUM, GOLD, PLATINUM, PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM,* IRIDIUM

MOLYBDENUM, Mo. At. Wt. 96.0, At. No. 42

Density 10.2. M. P. 2622 ± 10°

Occurrence. — Molybdenite, MoS_2; wulfenite, $PbMoO_4$; powellite, $CaMoO_4$. The mineral molybdenite has sometimes been mistaken for graphite which in turn has been called plumbago or "black lead." Molybdenum owes its name to the Greek word *molybdos* = lead.

Properties. — Metallic molybdenum when pure is silver white, tough, malleable, and softer than glass. It is not oxidized easily by air or water at ordinary temperatures, but it becomes brown, then blue, and finally white when heated above 600°; the final product of the oxidation is white MoO_3. As ferromolybdenum it is used in the manufacture of alloy steels like those for high-speed tools. This constitutes the principal commercial application of molybdenum, though smaller quantities are used in electric lamps and radio tubes. Molybdic acid anhydride, MoO_3, is used in the manufacture of dyes and inks and is an important chemical reagent. The metal dissolves in nitric acid, aqua regia, and concentrated sulfuric acid. Molybdenum has a valence of 2, 3, 4, and 6, and forms the following oxides: MoO, Mo_2O_3, MoO_2, and MoO_3. The first three are basic anhydrides; the last oxide, MoO_3, is an acid anhydride, forming a white mass (yellow when warm) which is readily fusible, but very difficultly volatile. When heated strongly, colorless, transparent, thin, orthorhombic plates of MoO_3 may be obtained from the fumes. MoO_3 is only very slightly soluble in water, but dissolves readily in alkalies and in ammonia, forming molybdates. Molybdic acid itself can be obtained as a solid mass by acidifying the solution of an alkali molybdate; it is soluble in an excess of acid (difference from tungstic acid). In the acid solutions, probably some hexavalent molybdenum cations are present. The most important commercial molybdate is acid ammonium molybdate, corresponding to the formula:

$$(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O \quad \text{or} \quad 3(NH_4)_2MoO_4 \cdot 4\,MoO_3 \cdot 4\,H_2O$$

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* It is difficult to group some of the rare elements consistently in the old qualitative arrangement. Treadwell places thallium, vanadium, molybdenum, and tungsten in this group, but there are objections to such a classification. In the qualitative scheme tungstic acid is similar to silicic acid, but in other respects tungstic and molybdic acids are similar. Selenium and tellurium are distinctly acidic in their compounds and really do not belong with the cations.

The alkali molybdates are soluble in water; the remaining salts are mostly insoluble in water but soluble in acids.

Reactions in the Wet Way

A solution of ammonium molybdate should be used.

1. **Dilute Acids** precipitate from concentrated alkali molybdate solutions white H_2MoO_4, soluble in an excess of acid.

Concentrated Sulfuric Acid. — If a trace of a molybdenum compound is evaporated with a drop of concentrated sulfuric acid almost to dryness in a porcelain dish, the mass is colored intensely blue. This is an exceedingly delicate reaction.

Antimony pentoxide, considerable stannic oxide, and other impurities interfere with this reaction.

2. H_2S at first colors acid molybdenum solutions blue, and precipitates, little by little, the molybdenum as brown molybdenum trisulfide, MoS_3, soluble in ammonium sulfide, forming a brown solution from which MoS_3 is reprecipitated by the addition of acids. The precipitation is best accomplished by saturating the acid solution with H_2S in a pressure flask, stoppering the flask and heating in a water bath. Molybdenum sulfide is oxidized by treatment with concentrated nitric acid, or by roasting in the air, into MoO_3.

3. $FeSO_4$ and sulfuric acid added to an acid solution of molybdate give a permanent blue color.

4. H_2O_2.—If a solution to be tested for molybdenum is evaporated to dryness on the water-bath, the residue treated with a little concentrated ammonia and then with hydrogen peroxide, the ammoniacal solution is immediately turned pink or red. Then, by evaporating to dryness again and treating the residue with sulfuric or nitric acid, yellow permolybdic acid, $HMoO_4$, is obtained.

5. **KCNS** causes no change when added to an acid solution of molybdate but if zinc or stannous chloride is also added, a blood red coloration is produced. The complex thiocyanate formed is usually assumed to be $K_3[Mo(CNS)_6]$ but more recent work favors the formula $K_2[MoO(SCN)_5]$ with quinquevalent rather than trivalent molybdenum. If the solution is shaken with ether, the red compound is extracted. Phosphoric acid does not interfere but tartaric acid does.

As little as 0.1 γ of molybdenum can be detected as follows: Place a drop of the solution to be tested on filter paper which has been moistened with hydrochloric acid to prevent interference of tungsten. Add a drop of KCNS reagent; if iron is present a red spot of $Fe(CNS)_3$ will appear, and will disappear on addition of a drop of $SnCl_2$ or of $Na_2S_2O_3$ when the red spot due to $K_3[Mo(CNS)_6]$ will appear.

6. **Lead Acetate** precipitates white lead molybdate, soluble in nitric acid.

7. **Mercurous Nitrate** precipitates yellow mercurous molybdate from neutral solutions; the precipitate is soluble in nitric acid.

8. **Phenylhydrazine,** $C_6H_5NH \cdot NH_2$, reacts with molybdates in the presence of acid to give a red precipitate or blood-red coloration. The phenylhydrazine is oxidized by molybdate to diazonium salt, and this couples with excess phenylhydrazine and molybdate to form a colored compound.

Place a drop of the solution to be tested on a spot plate and mix with a drop of a solution of phenylhydrazine in glacial acetic acid. A red coloration appears with 0.33 γ of molybdenum.

9. **Potassium Ferrocyanide** produces a reddish brown precipitate — a very sensitive test.

Molybdenum solutions containing free oxalic, acetic, or phosphoric acids usually give no precipitate with potassium ferrocyanide, but merely a brown coloration. Molybdenum ferrocyanide is insoluble in dilute mineral acids but is dissolved by concentrated hydrochloric acid and reprecipitated upon diluting. It is readily soluble in caustic alkali and ammonia solutions, in which respect it is different from the cupric and uranyl ferrocyanides (pp. 137 and 545). To detect the ferrocyanide ion in molybdenum ferrocyanide, dissolve the salt in ammonia, saturate the ammoniacal solution with H_2S, acidify with dilute H_2SO_4, filter off the MoS_3, and test the filtrate with ferric chloride solution (p. 334).

10. **Sodium Phosphate.**—If a few drops of a solution of sodium phosphate are added to a molybdate solution strongly acid with nitric acid, a yellow crystalline precipitate of ammonium phosphomolybdate is formed, slowly in the cold, but much more quickly on warming the solution (cf. Phosphoric Acid, p. 400). Arsenic acid causes the precipitation of a similar compound (cf. p. 149).

11. SO_2 does not reduce dilute, strongly acid solutions of molybdates either in the cold or on heating. Neutral or slightly acid solutions are reduced and colored blue.

12. **Zinc.**—If a molybdate solution which is acid with hydrochloric or sulfuric acid is treated with zinc, the solution is colored at first blue, then green, and finally brown. Other reducing agents such as $SnCl_2$, $Hg_2(NO_3)_2$, etc., cause the same reaction.

Reactions in the Dry Way

Alkali molybdates, alone or with sodium carbonate, are reduced on charcoal to gray molybdenum, a white incrustation of MoO_3 being formed at the same time.

Salt of Phosphorus Bead. — All molybdenum compounds color the bead, but the color depends upon the concentration. In the oxidizing

flame the hot bead is colored brownish yellow to yellow; it becomes yellowish green on cooling and finally colorless. In the reducing flame the bead becomes dark brown when hot and grass-green when cold. The borax bead is similar but not quite so characteristic.

SELENIUM, Se. At. Wt. 78.96, At. No. 34

Density 4.28–4.5. M. P. 217–220°. B. P. 690°

Occurrence. — Although selenium is quite widely distributed in nature, it is invariably found in very small amounts, usually replacing sulfur, forming isomorphous compounds with lead, silver, copper, and mercury; clausthalite, PbSe; berzelianite, $(Cu,Ag,Tl)_2Se$; naumannite, $(Ag_2,Pb)Se$; tiemannite, HgSe; lehrbachite, (Pb,Hg)Se; onofrite, Hg(Se,S); eucairite, $(Ag,Cu)_2Se$. It is also found in small amounts in many varieties of pyrite and chalcopyrite, and indeed the small quantities which are found in these minerals form the chief source of the selenium of commerce. By roasting these minerals (as in the manufacture of sulfuric acid) all the selenium is volatilized, and is subsequently deposited in the lead chambers as a mud from which it is extracted with a solution of potassium cyanide and afterwards precipitated with acid:

$$KCN + Se \rightarrow KCNSe \quad \text{and} \quad KCNSe + HCl \rightarrow HCN + KCl + Se$$

The name selenium comes from the Greek word *selene* = Moon. It was discovered by Berzelius in 1817.

Properties. — Selenium, like sulfur, exists in several allotropic forms. The vitreous modification, *α-selenium*, dissolves slowly but completely in carbon disulfide. Red *β-selenium* is obtained by reducing a cold solution of selenious acid with sulfurous acid; it is somewhat less soluble in carbon disulfide. The carbon disulfide solution of selenium reacts with metallic mercury and dark gray mercury selenide precipitates. By heating *red* selenium with hot water for some time, it is changed into *dark gray γ-selenium*, and is then *insoluble* in carbon disulfide. This is the most stable form, and all other modifications change into it.

On being heated in the air, selenium burns with a bluish flame (giving off an odor similar to that of rotten radishes), forming white, crystalline selenium dioxide, SeO_2, which will sublime on being heated in a stream of oxygen. Selenium forms one oxide SeO_2, and two acids: selenious acid, H_2SeO_3, and selenic acid, H_2SeO_4. The vapors of selenium dioxide are yellow.

When selenium is heated in hydrogen, gaseous hydrogen selenide, H_2Se, is formed which behaves like hydrogen sulfide in its reactions.

Selenious acid, H_2SeO_3, is obtained in the form of long, colorless needles by oxidizing selenium with nitric acid, concentrated sulfuric acid or aqua regia,* or by dissolving its anhydride, SeO_2, in water. Unlike sulfurous acid, it is not changed on standing in the air into selenic acid; but, on the contrary, is reduced by dust, etc., to red selenium. The acid is dibasic, and forms salts in which either one or both of the hydrogen atoms are replaced by metal.

The acid salts are all soluble in water, but all the neutral salts are insoluble with the exception of those of the alkalies.

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* If a solution of selenium in aqua regia is evaporated, considerable selenium is lost by volatilization; the addition of KCl or NaCl to the solution lessens such loss.

Selenic acid, H_2SeO_4, is obtained in solution by conducting chlorine into water which contains either suspended selenium or dissolved selenious acid:

$$Se + 3\ Cl_2 + 4\ H_2O \rightarrow H_2SeO_4 + 6\ HCl$$

Sodium selenate is obtained by fusing selenium with sodium carbonate and potassium nitrate. Selenic acid is a dibasic acid and behaves similarly to a peroxide, evolving chlorine when boiled with concentrated hydrochloric acid, being reduced to selenious acid:

$$H_2SeO_4 + 2\ HCl \rightarrow H_2O + H_2SeO_3 + Cl_2\uparrow$$

Noyes and Bray remove selenium as $SeBr_4$ together with $AsBr_3$ and $GeBr_4$ at the beginning of a qualitative analysis by using HBr as a solvent together with bromine. This furnishes a means of separating selenium from tellurium as well as from other elements.

The electrical conductivity of gray selenium is very low at room temperature or in the dark, but exposure to light or increase in temperature causes a marked lowering of the resistance. The action of the selenium photoelectric cell depends on this property the sensitivity being so great that under proper conditions the light from a star will produce an appreciable effect. Selenium is used in the glass industry to produce ruby-red glass, in fireproofing electric cables, in the rubber industry, and to some extent in steel making. Selenious acid has become an important chemical reagent; a small quantity of selenious acid greatly accelerates the destruction of organic matter with sulfuric acid prior to the Kjeldahl determination of nitrogen.

(*a*) *Selenious Acid*

Reactions in the Wet Way

A solution of either potassium selenite or of free selenious acid should be used.

1. **H_2S** produces a lemon-yellow precipitate, consisting of selenium and sulfur, from solutions in water or in dilute hydrochloric acid:

$$H_2SeO_3 + 2\ H_2S \rightarrow 3\ H_2O + Se + 2\ S$$

The precipitate is reddish yellow when formed in hot solutions. It is soluble in ammonium sulfide.

2. **$BaCl_2$** precipitates from neutral solutions white barium selenite. $BaSeO_3$, soluble in dilute acids.

3. **$CuSO_4$** produces a greenish-blue, crystalline precipitate (difference from selenic acid).

4. **Reducing Agents.**

$FeSO_4$ immediately precipitates selenium from concentrated solutions of selenious acid containing hydrochloric acid; from dilute solutions the precipitation takes place very slowly and incompletely if much sulfuric acid is present.

Hydrazine Hydrochloride precipitates selenium from hot acid and alkaline solutions; the selenium is red at first and finally gray.

Hydriodic Acid (KI and HCl) precipitates red selenium in the cold (difference from tellurium).

As little as 1 γ of selenium can be detected by the following spot test:

Place a drop of concentrated HI solution on a piece of white filter paper and add to it a drop of the acid solution to be tested. If Se is present a reddish brown spot is obtained and the color is not discharged by adding $Na_2S_2O_3$ solution.

Hydroxylamine Hydrochloride precipitates selenium from solutions of selenious acid containing sulfuric or hydrochloric acid, on long boiling; the precipitated selenium is red at first but finally becomes gray (difference from tellurium):

$$2\,NH_2OH + H_2SeO_3 \rightarrow Se + N_2O\uparrow + 4\,H_2O$$

SO_2 precipitates red selenium on long boiling; eventually the precipitate turns grayish black.

$SnCl_2$ precipitates red selenium even in the presence of considerable sulfuric acid.

Zinc precipitates red selenium from acid solutions: the zinc becomes coated with Se and looks as if covered with Cu.

5. **Thiourea,** $CS(NH_2)_2$, precipitates red Se from cold, dilute solutions. Place a little of the powdered reagent on filter paper and moisten with a drop of the solution to be tested; if 0.1 γ of selenium is present an orange-red spot will appear. Nitrates and larger quantities of copper interfere. Tellurium and bismuth give yellow precipitates.

(*b*) *Selenic Acid*

Reactions in the Wet Way

A solution of potassium selenate should be used.

1. **H_2S** causes no precipitation unless the solution is boiled with hydrochloric acid. In the latter case the selenic acid is reduced first to selenious acid and then to selenium, which precipitates together with free sulfur.

2. **$BaCl_2$** gives a white precipitate of barium selenate, $BaSeO_4$, insoluble in water and in dilute acids, soluble, with evolution of chlorine, on being boiled with hydrochloric acid:

$$BaSeO_4 + 4\,HCl \rightarrow BaCl_2 + H_2SeO_3 + Cl_2\uparrow + H_2O$$

3. **$CuSO_4$** produces no precipitation.

METHOD FOR TESTING SULFURIC ACID FOR SELENIUM*

Add 5 or 6 drops of the acid to be tested to a freshly prepared solution of a little codeine in sulfuric acid; if selenium is present, a green coloration will be apparent. The test is a very delicate one.

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* Dragendorff, *Chem. Zentralbl.*, **1900**, 944.

Reactions in the Dry Way

All selenium compounds emit the odor of decayed radishes on being mixed with sodium carbonate and heated on charcoal before the blowpipe.

If a selenium compound is heated at the end of a thread of asbestos in the upper reducing flame of the Bunsen burner, it will be reduced to selenium; and if a test tube filled with water is held above the flame, a red coating of selenium will be deposited upon the glass.* If a few drops of concentrated sulfuric acid † are placed in a larger test tube (large enough to hold the smaller test tube) and the tube on which the selenium is deposited is emptied and placed within the larger tube, the selenium will dissolve ‡ in the sulfuric acid, forming a green solution; but on the addition of water, red selenium will be reprecipitated (difference from tellurium):

$$\underset{\text{Green}}{SeSO_3} + H_2O \rightarrow Se + H_2SO_4$$

TELLURIUM, Te. At. Wt. 127.61, At. No. 52

Density 6.1-6.4. M. P. 452°. B. P. 1390°

Occurrence. — Tellurium is a rarer element than selenium, always occurring in the form of a telluride,§ and usually combined with the noble metals: calaverite, $(Au,Ag)Te_2$; krennerite, $(Au,Ag)Te_2$; sylvanite, a telluride of Ag and Au; nagyagite, a complex mineral containing Pb, Au, Sb, S and Te; coloradoite, HgTe; silver telluride, Ag_2Te; and often in small amounts in galena and copper ores. Emmonsite of Cripple Creek, Colorado, is a ferric tellurite with 70.71 per cent TeO_2 and 22.76 per cent Fe_2O_3.

Properties. — Tellurium itself is a bluish white, brittle substance, which can be distilled in a stream of hydrogen. It is stable in the air and in boiling water. It burns in the air with a bluish green flame, forming tellurium dioxide, TeO_2. It is insoluble in carbon disulfide and in hydrochloric acid but can be oxidized by means of nitric acid to tellurous acid. On being fused with potassium cyanide, out of contact with the air, it is changed to potassium telluride,

$$2\,KCN + Te \rightarrow K_2Te + (CN)_2\uparrow$$

which dissolves in water, forming a cherry-red solution. If air is conducted through this solution, the tellurium is precipitated in the form of a black powder (difference from selenium):

$$2\,K_2Te + 2\,H_2O + O_2 \rightarrow 4\,KOH + 2\,Te$$

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* Cf. page 78.

† The sulfuric acid should be freed from water by heating in a platinum crucible to a temperature just below the boiling point, and the crucible with its contents allowed to cool in a desiccator.

‡ Slowly in the cold, readily on warming.

§ These tellurides are sometimes regarded as tellurium alloyed with metal.

Tellurium may be separated from selenium by means of this last reaction. Fuse the two metals with potassium cyanide, extract the melt with water, and precipitate the tellurium by passing a current of air through the solution; precipitate the selenium from the filtrate by acidifying with hydrochloric acid. Tellurium forms two oxides: TeO_2 and TeO_3.

Tellurium gets its name from the Latin word *tellus* = earth. It was discovered by Reichenstein in 1782. It is used to some extent in ceramics and has been employed in steel making.

Tellurium dioxide (the anhydride of tellurous acid) is usually obtained in the form of a white mass, which melts on gentle heating, forming a yellow liquid. Tellurium dioxide does not sublime (difference from selenium). It is scarcely soluble at all in water, is slightly soluble in ammonia and in dilute acids, but readily soluble in concentrated acids or in caustic potash solutions. TeO_2 dissolves in fairly concentrated sulfuric acid, forming the basic sulfate, $Te_2O_3 \cdot SO_4$, while with nitric acid it forms the basic nitrate, $Te_2O_3(OH)NO_3$. Both these compounds are hydrolyzed readily, forming insoluble tellurous acid, which, in turn, loses water and forms the anhydride.

On dissolving TeO_2 in caustic potash, potassium tellurite, K_2TeO_3, is obtained. *Only the alkali tellurites are soluble in water.*

Tellurium trioxide (telluric anhydride) is formed by heating telluric acid. It is a yellow powder, insoluble in water and nitric acids, scarcely affected by boiling with concentrated hydrochloric acid, but readily dissolved by boiling with a concentrated solution of potassium hydroxide (but not by sodium hydroxide), forming potassium tellurate.

Telluric acid, $H_2TeO_4 \cdot 2\,H_2O$, is a very weak acid, obtained by oxidizing tellurous acid with chromic acid, and precipitating the telluric acid by the addition of concentrated nitric acid. The acid forms a colorless, crystalline mass, is readily soluble in water, and is converted by concentrated hydrochloric acid into tellurous acid, with evolution of chlorine. Telluric acid dissolves readily in caustic potash (or soda) solution, forming the readily soluble alkali tellurate, which reacts strongly alkaline in aqueous solution.

By gently heating the hydrated telluric acid, the anhydrous acid, H_2TeO_4, is obtained in the form of a white powder which is totally different from the hydrated acid. The latter is *soluble* in water and in caustic alkalies, and is *completely reduced* by boiling with concentrated hydrochloric acid; but the anhydrous acid is *insoluble* in water and in concentrated sodium hydroxide solution, and is only very slightly attacked by boiling, concentrated hydrochloric acid, although readily soluble in warm potassium hydroxide solution.

Only the alkali tellurates are soluble in water; the others are usually obtained in the form of amorphous precipitates soluble in acids.

(*a*) *Tellurous Acid*

Reactions in the Wet Way

A solution of potassium tellurite, K_2TeO_3, should be used.

1. H_2S precipitates from acid solutions brown TeS_2, which is readily soluble in ammonium sulfide. The precipitate decomposes easily into tellurium and sulfur.

2. **Reducing Agents.**

$FeSO_4$ reduces neither tellurous nor telluric acids (difference from selenium).

Hydrazine Hydrochloride precipitates black tellurium from both acid and ammoniacal solutions:

$$N_2H_4 \cdot 2\,HCl + TeO_3^{--} \rightarrow 3\,H_2O + N_2\uparrow + Te + 2\,Cl^-$$

Hydroxylamine Hydrochloride produces no precipitate in solutions of tellurous acid containing mineral acids, but precipitates tellurium completely by boiling the ammoniacal solutions for a long time.

$$2\,NH_2OH + TeO_3^{--} + 2\,H^+ \rightarrow 4\,H_2O + N_2O\uparrow + Te$$

Hydriodic Acid (KI and HCl) produces no precipitation, but merely a reddish brown coloration that turns light yellow on boiling (difference from selenium).

Hypophosphorous Acid precipitates tellurium from both tellurites and tellurates.

H_3PO_3 precipitates the tellurium only from concentrated solutions, not at all from cold dilute solutions.

SO_2 precipitates tellurium completely from *dilute* hydrochloric acid solutions in the form of a black powder, even in the presence of tartaric acid; but from a solution containing considerable hydrochloric acid no tellurium is precipitated even on boiling (difference from selenium). The separation of the selenium from tellurium can be accomplished in hydrochloric acid, density 1.18.

$SnCl_2$ or **Zn** causes black tellurium to precipitate from solutions which are not too acid. Alkali stannite solutions precipitate tellurium from both tellurous and telluric acid solutions.

Zinc (or Fe, Sb, Sn, Cd, Hg, Pb, Cu, etc.) precipitates black tellurium.

3. **Disodium Phosphate** and **Barium Chloride** give white precipitates.

4. **HCl** produces a white precipitate of H_2TeO_3.

5. **Magnesium Chloride** reagent gives a white, amorphous precipitate of magnesium tellurite. (With selenious acid a crystalline precipitate of magnesium selenite is formed.)

(*b*) *Telluric Acid*

Reactions in the Wet Way

A solution of potassium tellurate should be used.

1. **HCl** causes no precipitation; but if the solution is boiled chlorine is evolved, and on dilution with water tellurous acid is precipitated.

2. **H_2S** and reducing agents have the same effect upon hot solutions of tellurates as upon tellurites; in the cold, no precipitate is formed

(heavy metals can be separated from tellurium by hydrogen sulfide in the cold).

3. **Hydrazine Hydrochloride** precipitates all the tellurium as a black powder by long boiling of the acid or alkaline solution:

$$3(N_2H_4 \cdot 2\,HCl) + 2\,TeO_4^{--} \rightarrow 8\,H_2O + 2\,H^+ + 6\,Cl^- + 3\,N_2\uparrow + 2\,\mathbf{Te}$$

4. **Lead Salts** precipitate difficultly soluble lead tellurate.

Reactions in the Dry Way

Metallic tellurium is formed by heating any telluride in the upper reducing flame, and can be collected on the lower surface of a test tube, which is filled with water, in the form of a black film, soluble in concentrated sulfuric acid. The latter solution is of a carmine-red color (difference from selenium); on the addition of water black tellurium is deposited:

$$\underset{\text{Carmine red}}{TeSO_3} + H_2O \rightarrow \mathbf{Te} + H_2SO_4$$

GERMANIUM, Ge. At. Wt. 72.60, At. No. 32

Density 5.35. M. P. 916° in air, 958° in hydrogen; changes to GeO at 1250°

Occurrence. — Germanium was discovered by Clemens Winkler in 1886 in a mineral named argyrodite, $4\,Ag_2S \cdot GeS_2$, first studied by Welsbach in 1885. Winkler analyzed the mineral and succeeded in proving that it contained, besides silver and sulfur, about 6–7 per cent of a new element, the properties of which had been predicted as *eka-silicon* by Mendelejeff in his periodic classification of the elements. The element is found in a South African mineral called germanite but is most commonly obtained from the distillation residues obtained in the roasting of the zinc sulfide ores of Missouri and Wisconsin, although the ores themselves contain only about 0.01 per cent of germanium.

Properties. — Germanium belongs in the fourth group of the periodic classification lying between silicon and tin. Its oxide, GeO_2, forms with cold water a dilute colloidal solution which, on being heated, forms a true solution of slightly acid reaction, from which fact the existence of germanic acid, H_2GeO_3, can be assumed. Like stannic hydroxide, it is amphoteric and forms salts with both acids and bases.

Compounds. — Germanium sulfide, GeS_2, is a white, soft powder which can be obtained by passing hydrogen sulfide into the aqueous solution of the oxide. The sulfide is appreciably soluble in water and dissolves readily in alkali hydroxide or alkaline sulfide solutions. Germanium fluoride, GeF_4, is known as its hydrate, $GeF_4 \cdot 3\,H_2O$, which exists in hygroscopic crystals and as salts of H_2GeF_6. Germanium chloride, $GeCl_4$, is a liquid boiling at 75°, of density 1.87; it hydrolyzes slowly when in contact with water. Germanium bromide, $GeBr_4$, is colorless and boils at 186°. Germanium iodide, GeI_4, is a red powder which melts at 144°. Germanous chloride, $GeCl_2$, is a colorless liquid which fumes in the air and colors a cork stopper red. Its solution in hydrochloric acid is a strong reducing agent. Germanium chloroform, $GeHCl_3$, is obtained by passing HCl gas over gently heated, powdered germanium. It is a liquid which boils at 75° and has a density of 1.93.

It hydrolyzes with water to form $Ge(OH)_2$:

$$Ge + 3\,HCl \rightarrow GeHCl_3 + H_2\uparrow$$
$$GeHCl_3 + 2\,H_2O \rightarrow Ge(OH)_2 + 3\,HCl$$

In Noyes and Bray's *Qualitative Analysis for the Rare Elements*, the first solvent used is hydrobromic acid. About 1 g of solid is boiled with 10 ml of 9 *N* HBr for ten minutes, taking pains to pass the distillate into 5 ml of saturated Br_2 solution. Then the distillate and the Br_2 solution are poured back into the flask and the liquid is boiled until it is reduced to 3 ml. Under these conditions, practically all arsenic, selenium, and germanium are removed as $AsBr_3$, $SeBr_4$, and $GeBr_4$. The distillate is collected in 5 ml of saturated bromine water which is cooled by ice water.

To the distillate, molar $Na_2S_2O_3$ solution is added till the excess Br_2 is almost but not quite removed, and the selenium is precipitated as red Se by boiling with 1 ml of 3-molar hydroxylamine hydrochloride solution, $NH_2OH \cdot HCl$.

After the removal of the Se by filtration, the arsenic and germanium are precipitated as sulfides by means of H_2S. The sulfide precipitate is dissolved in 6–18 ml of 6 *N* NH_4OH in a platinum or Bakelite dish and two-thirds as much of 27 *N* HF is added. Then, on introducing H_2S again, a yellow precipitate of arsenic sulfide is obtained. The presence of hydrofluoric acid converts the germanium into H_2GeF_6 and the GeF_6^{--} ion is so stable that it does not react with H_2S although GeS_2 can be formed from solutions containing other mineral acids.

After the arsenic has been removed by filtration of the sulfide, the next step is to remove all fluoride by evaporating to fumes after adding 10 ml of 18 *N* H_2SO_4. Then by adding 25 ml of water and saturating with H_2S, a white precipitate of GeS_2 will form if any germanium is present.

The best confirmatory test for germanium consists in dissolving the GeS_2 precipitate in a platinum crucible with a little 3 *N* NH_4OH, evaporating to dryness and heating with HF which forms H_2GeF_6. If the solution is not clear it should be filtered from deposited sulfur, using a Bakelite funnel, and evaporated just to dryness to remove any silicon. Then by adding 10 drops of HF, 10 drops of 6 *N* K_2CO_3 solution, and 1 ml of water and heating to boiling, a viscous-appearing, grayish white, translucent precipitate of K_2GeF_6 will be obtained.

$$3\,GeS_2 + 6\,NH_4OH \rightleftarrows [GeO_3]^{--} + 2\,[GeS_3]^{--} + 6\,NH_4^+ + 3\,H_2O$$
$$GeS_2 + 6\,HF \rightleftarrows H_2GeF_6 + 2\,H_2S\uparrow$$

Germanium is likely to be mistaken for arsenic in the Marsh test (p. 151).

GOLD, Au. At. Wt. 197.2, At. No. 79

Density 19.33. M. P. 1063°

Occurrence. — Gold usually occurs native in quartz and in river sands; also as telluride of gold in sylvanite, $(AuAg)_2Te_3$, and in nagyagite, a complex mineral containing Pb, Au, Te, S and Sb, and is found in small amounts in many pyrite and other sulfide ores.

The element gold was known in prehistoric ages (before 4000 B.C.) and probably owes its name to the Sanskrit *jval* = to shine. About half the gold mined today comes from South Africa, and about one-quarter from the United States. Prior to 1934 the value of a Troy ounce of gold was set at $20.67, and this served as a standard for monetary values for many years. In 1928 the value of the gold mined was about $400,000,000. Gold is of yellow color when pure and melts without being oxidized.

It is not tarnished by water or hydrogen sulfide and is not dissolved by the acids of the laboratory when acting alone. For this reason gold has been called a *noble metal.* Gold is the most ductile of all metals, and may be hammered into exceedingly thin leaves, which are transparent, with a bluish green color.

Properties. — Commercial gold is usually alloyed with copper, with silver, or with both metals. Pure gold is designated as 24-carat gold or 1000/1000 fine. Fourteen-carat gold contains 14 parts of gold to 10 parts of other metal and 18-carat gold contains 18 parts of gold and 6 parts of alloy; the former, therefore, contains 58.3 per cent and the latter 75 per cent of pure gold.

The proper solvent for gold is aqua regia, but it is also soluble in bromine and chlorine water, forming a trihalogen compound:

$$2\,\mathbf{Au} + 2\,HNO_3 + 6\,HCl \rightarrow 4\,H_2O + 2\,NO\uparrow + 2\,AuCl_3$$
$$2\,\mathbf{Au} + 3\,Br_2 \rightarrow 2\,AuBr_3$$

Gold is not attacked by mineral acids. It is dissolved by potassium cyanide solution in contact with the oxygen of air. Gold forms two oxides: aurous oxide, Au_2O; and auric oxide, Au_2O_3.

Both of these are exceedingly unstable; on gentle ignition they lose oxygen and are changed to metal (a property common to all " noble " metals).

All gold salts are unstable; even the most stable salt of all, the chloride, $AuCl_3$, is changed by gentle ignition into yellowish white aurous chloride, AuCl:

$$AuCl_3 \rightarrow AuCl + Cl_2\uparrow$$

On stronger ignition the third atom of chlorine is lost, and the yellow metal itself is left behind.

Salts. — Aurous chloride, AuCl, is insoluble in water, but on being boiled with water for some time, or more slowly in the cold, it is changed to auric chloride with deposition of metal:

$$3\,\mathbf{AuCl} \rightarrow AuCl_3 + 2\,\mathbf{Au}$$

The solution obtained by dissolving gold in aqua regia always contains auric chloride, so that only the reactions of auric compounds are of interest to the analytical chemist. Auric chloride unites with hydrochloric acid, forming chlorauric acid,

$$AuCl_3 + HCl \rightarrow H[AuCl_4]$$

which yields beautifully crystalline salts.

From an aqueous solution containing very little excess HCl, $AuCl_3$ can be extracted by shaking with ether or with ethyl acetate. The latter reagent is preferable if it is desired to dissolve out both $AuCl_3$ and $HgCl_2$. By shaking the ethyl acetate extract with 3-normal NH_4Cl, nearly all the $HgCl_2$ and very little of the $AuCl_3$ can be made to pass into the aqueous layer; in this way gold and mercury can be separated from platinum metals and from one another.

Auric salts are mostly yellow and readily soluble in water. The sulfide is black and soluble only in aqua regia.

Reactions in the Wet Way

1. **Alkali Hydroxide** produces in concentrated solutions a reddish brown voluminous precipitate of auric hydroxide, soluble in an excess of the reagent:

$$AuCl_4^- + 3\,OH^- \rightarrow \mathbf{Au(OH)_3} + 4\,Cl^-$$
$$\mathbf{Au(OH)_3} + OH^- \rightarrow 2\,H_2O + [AuO_2]^-$$

If the bright yellow solution of potassium aurate is carefully acidified with nitric acid, a precipitate of reddish brown auric acid is thrown down, which is soluble in nitric acid, but is reprecipitated, for the most part, by diluting and boiling.

As a rule, potassium hydroxide yields no precipitate in solutions of gold chloride, because the gold solution is usually so dilute that the amount of alkali added is sufficient to form the aurate at once.

2. **Ammonia** throws down a yellowish mixture of gold iminochloride, Au(NH)Cl, and gold iminoamide, $Au(NH)NH_2$,

$$AuCl_3 + 3\ NH_3 \rightarrow 2\ NH_4Cl + \mathbf{Au(NH)Cl}$$
$$AuCl_3 + 5\ NH_3 \rightarrow 3\ NH_4Cl + \mathbf{Au(NH)NH_2}$$

which explodes in a dry condition on warming or by concussion (fulminating gold*).

The most important reactions for the detection of gold are those which depend upon the extreme readiness with which the auric compounds are reduced. Auric compounds are strong oxidizing agents.

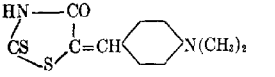
3. **Arsine** and **Stibine** precipitate gold completely:

$$2\ Au^{+++} + AsH_3 + 3\ H_2O \rightarrow H_3AsO_3 + 6\ H^+ + 2\ \mathbf{Au}$$

4. **Benzidine,** $C_{12}H_{10}(NH_2)_2$, is oxidized by trivalent gold salts to form a blue dyestuff (cf. p. 113). This test is very delicate and has been obtained with 0.02 γ of gold. Place a drop of the solution to be tested and a drop of 0.05 per cent solution of benzidine in 10 per cent acetic acid upon filter paper; a blue coloration is obtained if gold is present.

5. ***p*-Dimethylaminobenzylidinerhodanine** gives a red-violet precipitate. Silver, mercury, and palladium salts must be absent as they also form colored compounds with this reagent.

Moisten a piece of filter paper with a saturated solution of



in alcohol and dry. Upon the dry paper place a drop of the neutral or slightly acid solution to be tested. If 0.1 γ of gold is present a violet spot or ring will be obtained.

6. **Ferrous Sulfate** and **Oxalic Acid** both precipitate gold from neutral solutions even at room temperature (difference from platinum):

$$HAuCl_4 + 3\ Fe^{++} \rightarrow 3\ Fe^{+++} + H^+ + 4\ Cl^- + \mathbf{Au}$$
$$2\ HAuCl_4 + 3\ H_2C_2O_4 \rightarrow 8\ H^+ + 8\ Cl^- + 6\ CO_2\uparrow + 2\ \mathbf{Au}$$

* Raschig, *Ann. Chem. Pharm.*, **235**, 325 (1886).

7. **Formic Acid** precipitates gold from hot $HAuCl_4$ solution:

$$2\ HAuCl_4 + 3\ HCO_2H \rightarrow 3\ CO_2\uparrow + 8\ HCl + 2\ Au$$

Mercury, platinum, and palladium are also completely precipitated by this reagent and to some extent iridium, rhodium, and silver. These metals constitute the Gold Group in the analytical scheme of Noyes and Bray.

8. **Hydrogen Peroxide*** in alkaline solution immediately precipitates the gold as finely divided metal:

$$2\ Au^{+++} + 3\ H_2O_2 + 6\ OH^- \rightarrow 6\ H_2O + 3\ O_2\uparrow + 2\ Au$$

The precipitated metal appears brownish black by reflected light, but bluish green by transmitted light; 0.03 mg gold in 10 ml of liquid suffices to give a reddish coloration with a bluish shimmer.

9. **Hydrogen Sulfide** precipitates, in the cold, black gold disulfide from gold solutions:

$$2\ Au^{+++} + 3\ H_2S \rightarrow 6\ H^+ + S + Au_2S_2$$

Gold disulfide is insoluble in acids; but is readily soluble in aqua regia, forming auric chloride, $AuCl_3$.

The disulfide is difficultly soluble in ammonium sulfide, but more readily soluble in potassium polysulfide, forming a thio-salt:

$$Au_2S_2 + K_2S_2 \rightarrow 2\ KAuS_2$$

From this solution hydrochloric acid precipitates a yellowish brown sulfide:

$$2\ KAuS_2 + 2\ H^+ \rightarrow 2\ K^+ + H_2S + Au_2S_3(?)$$

From a hot solution, hydrogen sulfide precipitates brown, metallic gold:

$$8\ Au^{+++} + 3\ H_2S + 12\ H_2O \rightarrow 30\ H^+ + 3\ SO_4^{--} + 8\ Au$$

The finely divided metallic gold is soluble in hot potassium or sodium polysulfide, forming a thio-salt:

$$2\ Au + K_2S_4 \rightarrow 2\ KAuS_2$$

10. **Potassium Iodide** added to a dilute, alkaline solution causes precipitation of gold. This test is recommended by Noyes and Bray:

$$2\ Au^{+++} + 6\ I^- \rightarrow 3\ I_2 + 2\ Au$$

11. **Stannous Chloride** causes the following reaction to take place:†

$$2\ Au^{+++} + 3\ Sn^{++} \rightarrow 3\ Sn^{++++} + 2\ Au$$

If the solution tested is strongly acid with hydrochloric acid, the precipitate is pure gold and has the characteristic dark brown color of the finely divided metal.

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* Vanino and Seemann, *Ber.*, **1899**, 1968.

† Theodor Döring, *Chem. Zentralbl.*, **1900**, I, p. 735.

In very dilute weakly acid solutions the so-called purple of Cassius is thrown down, which consists of colloidal gold and tin hydroxide.*

Purple of Cassius is soluble in ammonia and in dilute caustic potash solution, forming reddish liquids. These solutions when cold remain clear for a long time and can even be boiled without decomposition. As the solution is concentrated a flocculent precipitate is formed which will dissolve on the addition of more ammonia.

The brown coloration can be distinctly seen if 0.3 mg gold is dissolved in 100 ml of the solution; if less than 0.3 mg of gold is present, only a yellowish coloration is obtained.

12. **Sulfurous Acid** reduces gold solutions:

$$2\ Au^{+++} + 3\ SO_2 + 6\ H_2O \rightarrow 12\ H^+ + 3\ SO_4^{--} + 2\ Au$$

13. **Zinc.** — The following gold test is very sensitive:† To a few drops of a dilute gold solution add a few drops of arsenic acid, two or three drops of ferric chloride solution, and two to three drops of hydrochloric acid. Dilute the mixture to 100 ml, and drop in a piece of zinc. Around the zinc the solution assumes a purple color, which, by moving the zinc in the solution, is disseminated through it, making it appear pink or purple. If the solution contains 0.03 mg of gold, within fifteen minutes a beautiful reddish color will be noticed.

Besides the above reagents many others, such as **formaldehyde** in the presence of alkali, **hydrazine sulfate,** etc., are capable of reducing gold from its solutions.

DETECTION OF GOLD IN ALLOYS AND ORES

On account of its softness, gold is always alloyed with silver and copper when used for coins or for jewelry. If such an alloy is treated with nitric acid, the copper and silver are dissolved and the gold usually remains as a brownish powder. To prove the presence of gold, filter through a small filter, dry the filter, roll up the paper, and wrap a platinum wire around it. Set fire to the paper and allow it to burn quietly. The ash must not be too strongly heated, for the gold would then melt and alloy with the platinum wire. Melt the ash with a little sodium carbonate on a charcoal stick; a gold button forms with the characteristic yellow color. The gold button can be pressed into a leaf in the agate mortar, transferred to a watch glass, and dissolved in a little aqua regia, forming auric chloride. Carefully evaporate the solution to dryness, dissolve the residue in a little water, add a dilute solution of stannous chloride, and the presence of gold is shown by the formation of the purple of Cassius. The hydrogen peroxide and zinc tests are still more delicate.

If it is a question of detecting very small amounts of gold (as in many copper coins), the above method is unsuitable. In such tests, extract the gold and silver by scorification and cupellation. Melt 5 to 10 g of the auriferous copper (or more in some cases) with 120 g of pure lead in a flat dish of infusible stone (a scorifying-dish), in a muffle with access of air. The copper and a part of the lead are oxi-

* Zsigmondy, *Ann. Chem. Pharm.*, **301**, 361 (1898).

† *Pharm. Chem. Zentralbl.*, **27**, 321.

dized, and the oxide unites with the silica of the dish to form a readily fusible slag, which eventually covers the unaffected lead and the dissolved silver and gold. This operation is known as *scorification*. When this point is reached, pour the molten mass into an iron scorification pan, previously well chalked. As soon as the mass becomes cool, remove it from the pan, and hammer the slag from the enclosed lead button and weigh the latter. Then put it on a *cupel* (a sort of crucible made of bone ash), of about the same weight as the lead button or a little heavier. Place the cupel in the muffle and again heat with ready access of air. The lead melts and is oxidized; the resulting lead oxide melts at 980° C and is partly absorbed by the porous cupel and partly volatilized, leaving a kernel of silver and gold behind. Flatten the metallic kernel to foil and treat it with 6-normal nitric acid, which dissolves the silver, leaving the gold, usually in the form of powder. Filter off the gold, dry, and melt it, as above described, upon the charcoal stick. If the alloy of gold and silver (obtained after cupellation) contains three parts of silver to one part of gold, the gold remains after separation with nitric acid as a thin, coherent, brownish mass which becomes hard on igniting, with the characteristic gold color. If the proportion of silver to gold is greater than 3 : 1, the separation by means of nitric acid will be complete and the gold will be left as a powder. If the ratio of silver to gold is less than 3 : 1, the separation by means of nitric acid is incomplete, and the gold residue usually appears yellow, and still contains some silver. In this case, add more silver with 1 g of lead and subject the mixture once more to cupellation, when the subsequent separation by means of nitric acid will be complete.

In order to detect very small amounts of gold in ores, a similar procedure is used.

If a muffle furnace is not available, the more tedious wet process must be used. For example, if it is desired to detect the presence of gold in pyrites, roast a large amount of the ore in the air until all the sulfur has been burned off, then treat with bromine water, and allow to stand twelve hours. Filter the solution (which now contains all the gold as auric bromide), and boil off the excess of bromine. Add ferrous sulfate and a little sulfuric acid, boil the solution again, and filter through a small filter. Wash the residue on the filter, dry, and then melt it on the charcoal stick.

By the above methods a fractional part of a milligram of gold can be detected with certainty.

Reactions in the Dry Way

All compounds of gold, when heated with soda on the charcoal stick, yield a malleable, metallic button, soluble only in aqua regia. The solution in the latter reagent should be evaporated, the residue dissolved in water and tested with stannous chloride, hydrogen peroxide, zinc, or potassium iodide.

THE PLATINUM METALS

PLATINUM, PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM, AND IRIDIUM

PLATINUM, Pt. At. Wt. 195.23, At. No. 78

Density 21.5. M. P. 1771°

Occurrence. — Platinum is found free in nature, usually accompanied by the other so-called platinum metals.

Properties. — The element platinum, which is much more valuable than gold, was discovered by Scaliger in 1558. It owes its name to the Spanish word *platina* = small silver. It is a grayish white metal which appears grayish black in a finely divided state (platinum black). When pure it is softer than silver, but it is hardened by other metals, particularly iridium. It is somewhat less ductile than gold or silver. Platinum sponge is formed by the ignition of ammonium chloroplatinate. The finely divided forms of platinum, platinum black, and platinum sponge, have a marked catalytic effect upon numerous reactions such as the hydrogenation of oils, contact process for making sulfuric acid from SO_2 and oxygen, oxidation of alcohol and many other organic compounds, union of hydrogen with chlorine, etc. The metal is not ordinarily attacked by mineral acids; it dissolves in aqua regia, forming chloroplatinic acid, $H_2[PtCl_6]$ (not platinum chloride, $PtCl_4$). By boiling concentrated sulfuric acid in platinum dishes 10 ml of acid will dissolve 3.8 mg of platinum in ten minutes. If the platinum is alloyed with sufficient silver, it dissolves in nitric acid, forming a brown solution. Like tin, platinum forms two oxides: platinum monoxide, PtO, and platinum dioxide, PtO_2.

Compounds. — Both oxides may be obtained by the careful ignition of the corresponding hydroxides. They are exceedingly unstable, being decomposed by gentle ignition into metal and oxygen; all the remaining platinum compounds behave similarly.

The most important of the platinum compounds are the chlorides. By dissolving platinum in aqua regia, chloroplatinic acid is always obtained, from which the di- and tetrachlorides may be derived; these unite with hydrochloric acid to form complex acids:

$PtCl_4 + 2\ HCl \rightarrow H_2[PtCl_6]$ (Chloroplatinic acid — orange-red crystals)

$PtCl_2 + 2\ HCl \rightarrow H_2[PtCl_4]$ (Chloroplatinous acid — known only in solution)

The aqueous solution of chloroplatinic acid is yellowish orange; a solution of chloroplatinous acid, containing the same quantity of platinum, is dark brown.

The potassium and ammonium salts of chloroplatinous acid are soluble in water; the corresponding salts of chloroplatinic acid are difficultly soluble in water and insoluble in 75 per cent alcohol.

Reactions in the Wet Way

A solution of chloroplatinic acid should be used for these reactions.

1. **Alkali Iodides** give a brownish red coloration due to the formation of the less ionized $[PtI_6]^{--}$.

$$[PtCl_6]^{--} + 6\ I^- \rightarrow [PtI_6]^{--} + 6\ Cl^-$$

2. **Ammonium** and **Potassium Chlorides** produce in concentrated solutions yellow precipitates (cf. pp. 281 and 291):

$$[PtCl_6]^{--} + 2\ K^+ \rightarrow \mathbf{K_2[PtCl_6]};\ [PtCl_6]^{--} + 2\ NH_4^+ \rightarrow \mathbf{(NH_4)_2[PtCl_6]}$$

This reaction is used to separate platinum and iridium from gold, palladium, and rhodium. To determine whether any yellow K_2PtCl_6 or black K_2IrCl_6 is present in a reddish precipitate produced by NH_4Cl, treat the precipitate with 10 ml of concentrated HCl and 0.5 ml of concentrated HNO_3 for fifteen minutes at 90°, adding a little more HNO_3 from time to time. Evaporate on the steam bath until no acid smell is apparent; add 5 ml of water and 2 ml of molar $NaHCO_3$ solution. Heat on the steam bath five minutes and add more $NaHCO_3$ if the solution is not alkaline to litmus. Cool somewhat; add 1 ml of bromine water and a little more bicarbonate. Heat ten minutes on the steam bath. The NaBrO formed will cause the precipitation of the iridium as black IrO_2. Filter, make acid with HCl, evaporate to dryness, and repeat the test with NH_4Cl, to see if any platinum is present.

3. **Carbon Monoxide**, on being passed into a solution of chloroplatinic acid containing sodium acetate, colors the solution a beautiful red owing to the formation of colloidal platinum (difference from palladium). After standing some time all the platinum is precipitated as a black powder and the supernatant liquid is colorless:

$$H_2[PtCl_6] + 2\,CO + 6\,C_2H_3O_2^- + 2\,H_2O \rightarrow 6\,Cl^- + 6\,HC_2H_3O_2 + 2\,CO_2\uparrow + \mathbf{Pt}$$

4. **Ferrous Salts** do not reduce chloroplatinic acid in the presence of acids (difference from gold), but cause precipitation of all the platinum (on warming) in a solution which has been neutralized with sodium carbonate:

$$[PtCl_6]^{=} + 6\,CO_3^{=} + 4\,Fe^{++} + 6\,H_2O \rightarrow 6\,CO_2\uparrow + 6\,Cl^- + 4\,\mathbf{Fe(OH)_3} + Pt$$

5. **Formaldehyde** in alkaline solutions precipitates the platinum as extremely finely divided *platinum black:*

$$H_2[PtCl_6] + HCHO + 6\ OH^- \rightarrow CO_2\uparrow + 6\ Cl^- + 5\ H_2O + \mathbf{Pt}$$

The precipitate may be washed with alkali salt solutions, but with pure water a black colloidal solution of platinum is formed.

6. **Formic Acid** precipitates from neutral, boiling solutions all the platinum in the form of a black powder:

$$H_2[PtCl_6] + 2\ \underset{\text{Formic acid}}{HCO_2H} \rightarrow 6\ HCl + 2\ CO_2\uparrow + \mathbf{Pt}$$

An acid solution must be neutralized with sodium carbonate before making this test.

7. **Glycerol** and **Sodium Hydroxide** reduce chloroplatinic acid on warming, with the separation of black, pulverulent metal:

$$C_3H_5(OH)_3 + 3\,[PtCl_6]^{=} + 16\,OH^- \rightarrow 18\,Cl^- + CO_3^{=} + C_2O_4^{=} + 12\,H_2O + 3\,Pt$$

8. **Hydrazine Hydrochloride,** $N_2H_4 \cdot 2\,HCl$, readily reduces chloroplatinic acid in ammoniacal solutions; some of the platinum is deposited as a mirror upon the sides of the vessel containing the solution:

$$(NH_4)_2[PtCl_6] + N_2H_4 \cdot 2\,HCl + 6\,NH_3 \rightarrow 8\,NH_4Cl + N_2\uparrow + Pt$$

9. **Hydrogen Sulfide** precipitates dark brown platinum disulfide very slowly in the cold, but quickly on warming:

$$H_2[PtCl_6] + 2\,H_2S \rightarrow 6\,HCl + PtS_2$$

Platinum sulfide is insoluble in mineral acids, but readily soluble in aqua regia. It is difficultly soluble in alkali monosulfide solutions, but more readily soluble in alkali polysulfides, forming a thio-salt, which is decomposable by acids, with precipitation of platinum sulfide.

10. **Oxalic Acid** does not precipitate platinum. Hydroxylamine in acid solution and in sodium hydroxide solution, **acetylene,** and **hydrogen peroxide** also fail to precipitate platinum (difference from gold).

11. **Stannous Chloride** reduces chloroplatinic acid to chloroplatinous acid; the solution becomes deep red.

$$[PtCl_6]^{--} + Sn^{++} \rightarrow Sn^{++++} + 2\,Cl^- + [PtCl_4]^{--}$$

12. **Zinc, cadmium, magnesium,** or **aluminum** reduces chloroplatinic acid to metal:

$$H_2[PtCl_6] + 3\,Zn \rightarrow 3\,ZnCl_2 + H_2\uparrow + Pt$$

The precipitated metal is in such a finely divided condition that it tends to run through the filter, especially on being washed with pure water; by washing with salt solution a clear filtrate can be obtained.

Reactions in the Dry Way

All platinum compounds, when heated with soda on charcoal, are reduced to the gray, spongy metal, which assumes a metallic luster on being rubbed with a pestle in an agate mortar. It can be distinguished from gold by its color, and from lead, tin, and silver by its infusibility and insolubility.

Separation of Gold from Platinum

Precipitate the platinum from a concentrated solution with a solution of ammonium chloride; filter, and treat the solution with ferrous sulfate to precipitate the gold.

According to Noyes and Bray, the separation of gold from platinum is best effected as follows: Evaporate the aqua regia solution to a volume less than 1 ml but take care not to overheat the residue. Add 12 ml of water, boil, and filter if necessary. Add 1 drop of 6 *N* HCl and shake vigorously with 10 ml of pure ethyl acetate in a separatory funnel. Draw off the aqueous layer and shake it with a fresh portion of ethyl acetate. Practically all the gold chloride will dissolve in the organic solvent and none of the platinum. Evaporate the combined ethyl acetate extracts to dryness in a porcelain dish on a steam bath and heat to barely visible redness. Cool, add 1 ml of 12 *N* HCl and a few drops of concentrated HNO_3. Evaporate nearly to dryness, add 5 ml of water and 2 ml of 6 *N* NaOH, and heat to boiling. Finely divided gold will be precipitated and a purple color is evident with 0.2 mg of Au. Take the aqueous solution from the ethyl acetate extraction, evaporate nearly to dryness, add 1 ml of water, and again evaporate on the water bath until the residue does not smell acid. Add 2 drops of 6 *N* HCl, not more than 1 ml of water, and powdered NH_4Cl until no more will dissolve on stirring or shaking. Cool in ice water. If 0.3 mg of Pt is present a noticeable precipitate of K_2PtCl_6 will be obtained.

PALLADIUM, Pd. At. Wt. 106.7, At. No. 46

Density 11.8. M. P. 1550°. B. P. 2200°

Occurrence. — The platinum metals form an isodimorphous group, but only in the case of palladium are both forms known — the isometric and the hexagonal:

(*a*) Isometric System.	(*b*) Hexagonal System.
Platinum (Pt, Fe).	Iridosmium (Sysserskite) (Ir, Os).
Iridium (Ir, Pt).	Osmiridium (Newjanskite) (Ir, Os,
Platinum-iridium (Pt, Ir, Rh).	Pt, Rh, Ru) or (Os, Ir, Rh).
Palladium (Pd, Pt, Ir).	**Palladium** (Pd, Pt, Ir).

Palladium is always present in platinum ores.

Properties. — Rolled, hammered, or cast palladium possesses an almost silver-white color, but when precipitated from solutions it is in the form of a black powder. It softens at temperatures considerably below the melting point and can be welded easily. If it is suspended in water when in the finely divided form, it is transparent with a reddish color. Palladium has the lowest melting point of all the platinum metals. On being heated in the air, it appears bluish, owing to the formation of Pd_2O; the latter, however, is decomposed by stronger heating. Palladium is grouped with ruthenium and rhodium in the periodic table (p. 87) and is, therefore, considered a platinum metal, but in its reaction toward acid it is very different. Much of the "platinum" in dental alloys is palladium.

Finely divided palladium has the very characteristic property of being able to absorb almost 700 times its own volume of hydrogen, and possesses consequently

a very strong catalytic action. If hydrogen and oxygen (air) are conducted at the same time over some gently ignited, finely divided, metallic palladium, the hydrogen is burnt to water, and in the same way carbon monoxide may be changed to carbon dioxide. Methane, however, is decomposed only by igniting the palladium more strongly, so that this gives us a method for separating methane from a mixture of H_2 and CO (cf. Vol. 2, Gas Analysis).

Colloidal palladium preparations show marked catalytic effects. Thus, by passing hydrogen gas into solutions of unsaturated organic compounds, a direct reduction (hydrogenation) often takes place if a little colloidal palladium is present.

Palladium forms two oxides, both of which possess basic properties: PdO and PdO_2. From the former the palladous, and from the latter the palladic, compounds are derived. The palladous compounds are much more stable than the palladic compounds, and the latter constantly exhibit the tendency to change into the former.

Behavior toward Acids. — Although the other platinum metals are attacked by no acid except aqua regia, palladium is dissolved slowly by hot nitric acid (also in the cold when it is alloyed with other metals such as Cu, Ag, etc.), forming a brown solution of $Pd(NO_3)_2$.

Finely divided, precipitated palladium is soluble in hydrochloric acid when exposed to the action of air at the same time, and less readily soluble in sulfuric acid. It is readily attacked by fusing with potassium pyrosulfate, forming soluble palladium sulfate, $PdSO_4$.

The best solvent for palladium is aqua regia.

By dissolving finely divided palladium in hydrochloric acid, palladous chloride is formed; or, better, by dissolving the metal in aqua regia, in which case a mixture of palladous and palladic chlorides is at first obtained. If this solution, however, is evaporated to dryness, palladic chloride loses chlorine and is completely changed into palladous chloride, so that on treating the residue with water a solution of palladous chloride is obtained. Since palladic chloride is decomposed completely by evaporation, it is evident that palladic chloride cannot exist in hot solutions.

(*a*) *Palladous Compounds*

Reactions in the Wet Way

Use a solution of palladous chloride, $PdCl_2$.

1. **Acetylene** precipitates palladous acetylide, which is soluble in ammonia, potassium cyanide, and sodium bisulfite solutions.

2. **Dimethylglyoxime** gives a yellow precipitate easily dissolved by ammonia or potassium cyanide solution; the precipitate is only slightly soluble in 50 per cent alcohol and dilute acids. Gold and platinum interfere as their salts are reduced to metal, but the other platinum metals do not interfere.

By this reaction Pd can be precipitated in 0.8–0.9-normal HCl in the presence of Pt which remains in solution.

3. **$Hg(CN)_2$** produces a yellowish white gelatinous precipitate of palladous cyanide, $Pd(CN)_2$, difficultly soluble in HCl, readily soluble in KCN and NH_3. On being ignited, the spongy metal remains.

The following spot test is said to permit the detection of 0.05 γ of palladium. To prevent interference of gold and platinum, the palladium is first precipitated as yellow $Pd(CN)_2$.

Upon a piece of filter paper, place a drop of saturated mercuric cyanide solution, a drop of the solution to be tested, and then another drop of mercuric cyanide solution. The palladium will be precipitated in the center of the spot while Au and Pt are farther off, and, by means of a drop of water can be washed away entirely. If now a drop of stannous chloride solution is added, a dark orange or gold-yellow coloration will appear in the center if palladium is present.

4. **HI** or **KI** produces a black precipitate of palladous iodide, PdI_2, even in very dilute solutions. The precipitate is insoluble in water, alcohol, ether, and HI, but soluble in KI and NH_3 to a reddish-brown solution.

5. **H_2S** precipitates black palladous sulfide from acid and neutral solutions. The precipitate, PdS, is insoluble in ammonium sulfide, but soluble in boiling hydrochloric acid, or more readily in aqua regia.

Palladous sulfide is soluble in potassium thiocarbonate solution and is not reprecipitated by means of carbon dioxide. (Lead sulfide does not dissolve in potassium thiocarbonate, and mercury sulfide is reprecipitated by carbon dioxide.)

6. **KCl**, when added to a concentrated solution, causes the precipitation of difficultly soluble, reddish brown $K_2[PdCl_4]$.

7. **KCNS** gives no precipitate with palladium solutions (difference from copper).

8. **KNO_2** gives a yellow, crystalline precipitate in solutions which are not too dilute.

9. **KOH** or **NaOH** precipitates a brown basic salt, soluble in an excess of the reagent. If the solution is acidified with HCl, then KOH produces no precipitate (difference from platinum). The precipitation of brown basic salt is complete by boiling a solution which has been neutralized with $NaHCO_3$ to $p_H = 6$.

10. **Na_2CO_3** produces a brown precipitate of palladous hydroxide, $Pd(OH)_2$, soluble in excess but reprecipitated on boiling.

11. **NH_4Cl.** — If a solution of palladous chloride or of sodium chloropalladite is treated with ammonium chloride and evaporated to dryness on the water bath, the residue is soluble in a very little water. If the solution is acidified with nitric acid, gradually all the palladium is precipitated as red $(NH_4)_2[PdCl_6]$ (difference from platinum).

12. **NH_4OH** gives a flesh-colored precipitate of $[Pd(NH_3)_2Cl_2]_n$*, soluble in an excess of ammonia, forming a colorless solution, containing tetramminepalladous chloride, $[Pd(NH_3)_4]Cl_2$, from which yellow crys-

* This compound is an isomer of dichlorodiamminepalladium, and is sometimes written thus: $PdCl_2 \cdot Pd(NH_3)_4Cl_2$.

talline dichlorodiamminepalladium, $Pd(NH_3)_2Cl_2$, is precipitated on the addition of hydrochloric acid. The latter compound is difficultly soluble in dilute hydrochloric acid and is used for the preparation of pure palladium.

In a solution of palladous nitrate, ammonia causes no precipitation, but forms colorless tetramminepalladous nitrate, $[Pd(NH_3)_4](NO_3)_2$.

13. **α-Nitroso-β-naphthol** (a saturated solution in 50 per cent acetic acid) gives a voluminous, brown precipitate of $Pd(C_{10}H_6NO_2)_2$ even in the most dilute solutions (difference from platinum).

14. **Reducing Agents.** — H_2SO_3, HCOOH, Zn, Fe, $FeSO_4$, Cu_2Cl_2,* alcohol, and CO† reduce palladium salts to the metal itself.

In the presence of HCl, stannous chloride forms at first a red, then a brown, and finally a green, solution; but in the absence of the acid, $SnCl_2$ causes a partial reduction to the metal and the solution turns green. Shaking with silver or mercury causes the precipitation of metallic palladium.

(*b*) *Palladic Compounds*

These give the same reactions as palladous compounds, on account of being readily changed into them. The most characteristic reaction is based upon the insolubility of the ammonium salt of chloropalladic acid. If a concentrated, cold solution of palladous chloride is shaken with chlorine water and then treated with ammonium chloride, a red crystalline precipitate of $(NH_4)_2[PdCl_6]$ is soon formed.

Reactions in the Dry Way

All palladium compounds are decomposed on ignition, leaving behind the metal, which is soluble in nitric acid or in aqua regia, and the solution thus obtained can be tested by the above reactions.

RHODIUM, Rh. At. Wt. 102.91, At. No. 45

Density 12.5. M. P. about 1985°

Properties. — Rhodium, which takes its name from the Greek *rhodon* = rose, was discovered by Wollaston in 1804. It possesses the color and luster of aluminum,

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* In the presence of considerable NaCl or HCl there is no reduction with Cu_2Cl_2.

† $PdCl_2 + CO + H_2O \rightarrow 2\,HCl + CO_2\uparrow + Pd$. This reaction enables one to detect small amounts of CO in gas mixtures, *e.g.*, in the air. For this purpose the gas is led through a narrow glass tube into 10 ml of a solution which contains 1 mg of $PdCl_2$ and 2 drops of dilute HCl. If CO is present, black Pd will be deposited, and the solution will become decolorized little by little. (Potain and Drouin, *Compt. rend.*, **126**, 938.) If too much HCl is present the reduction will not take place unless $NaC_2H_3O_2$ is added.

is more infusible than platinum, and melts at about 1985°; on cooling, the hot metal sputters and appears bluish, owing to oxidation. The solubility of rhodium depends entirely upon the fineness of the material; a platinum rhodium alloy is harder and more durable than pure platinum.

When precipitated from a solution of its chloride, by means of formic acid or other reducing agents at a temperature not exceeding 100°, it exists in an extremely finely divided state (rhodium black) and dissolves readily in boiling, concentrated sulfuric acid, or more readily in aqua regia. If, however, the finely divided metal is ignited strongly, it becomes (like the compact metal) almost insoluble in aqua regia.

The solution in aqua regia contains $RhCl_3$ which, like $CrCl_3$, exists in two modifications of greatly different solubility.

If rhodium is alloyed with large amounts of other metals (Pb, Zn, Bi, Cu, etc.), it is left in a finely divided condition after treatment of the alloy with acids, and is consequently soluble in aqua regia. When it is alloyed with much platinum or palladium a considerable amount of rhodium will dissolve in aqua regia; but when it is alloyed with a little platinum, most of the rhodium and a part of the platinum remain undissolved.

On being fused with potassium pyrosulfate, potassium rhodium sulfate is formed, which dissolves in water, forming a yellow solution, but becomes red on the addition of HCl.

Rhodium forms three oxides: rhodous oxide, RhO; rhodic oxide, Rh_2O_3; and rhodium peroxide, RhO_2; all possessing well-defined basic natures. The sesquioxide, Rh_2O_3, alone* forms a series of salts in which the rhodium is in the anion, of which sodium chlororhodite is the most important for the analytical chemist; when in this form it is easiest to bring rhodium into solution. This salt is prepared by mixing the finely divided metal very intimately with twice as much dry sodium chloride, placing it in a porcelain boat, and gently igniting it in a current of moist chlorine gas. The salt thus formed has the composition $Na_3[RhCl_6]$ and is soluble in water (45 parts of water dissolve 1 part of the salt). From this solution large, dark red, glistening triclinic prisms of $Na_3[RhCl_6] \cdot 9\ H_2O$ can be crystallized out.

Reactions in the Wet Way

Use a solution of sodium chlororhodite, $Na_3[RhCl_6]$.

1. **H_2S** precipitates (very slowly in the cold, but much more quickly on warming) black rhodium sulfide, Rh_2S_3 or $Rh(SH)_3$, insoluble in $(NH_4)_2S$, soluble in strong nitric acid, bromine, or aqua regia. Alkali monosulfide added in excess precipitates rhodium alkali sulfide, decomposable by water.

2. **KOH** and **NaOH** produce at first no precipitate; but after standing some time a yellow precipitate of rhodium hydroxide, $Rh(OH)_3 \cdot H_2O$, separates out. The precipitate is soluble in an excess of the reagent, but it is reprecipitated on boiling in the form of brownish black $Rh(OH)_3$.

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* A sodium rhodium sulfite of the formula $4\ RhSO_3 \cdot 6\ Na_2SO_3 \cdot 9\ H_2O$ was prepared by Bunsen.

In a solution of potassium rhodium sulfate, KOH precipitates the yellow compound immediately.

On adding KOH to a solution of rhodium chloride, at first no precipitate is produced; but on the addition of a little alcohol brownish black rhodium hydroxide is deposited.

3. **KNO_2**, on being warmed with sodium rhodium chloride solution, causes the precipitation of difficultly soluble, orange-yellow $K_3[Rh(NO_2)_6]$, soluble in HCl.

If $NaNO_2$ is used, soluble $Na_3Rh(NO_2)_6$ is formed which does not react with dilute NaOH solution. Iridium behaves similarly, and in this way rhodium and iridium can be separated from the copper group.

If the solution of $Na_3Rh(NO_2)_6$ and $Na_3Ir(NO_2)_6$ is evaporated to dryness with hydrochloric acid, avoiding too high a temperature, these complex nitrites are decomposed and Na_3IrCl_6 and Na_3RhCl_6 are formed. If these are heated with a dilute solution of sodium carbonate, soluble $NaIrO_2$ (sodium iridite) and insoluble, light-yellow $Rh(OH)_4$ are formed; then on adding a little liquid Br_2 and more sodium carbonate, bluish black IrO_2 and green RhO_2 are precipitated. The precipitated IrO_2 and RhO_2 can be dissolved in a little 9 *N* HBr which has a strong reducing action, and by evaporating the resulting solution with HCl and HNO_3, the iridium and rhodium are obtained as H_2IrCl_6 and H_3RhCl_6. To make sure that all the Ir is quadrivalent it is well to add HCl, evaporate again, and treat with HCl and Cl_2. Then on adding considerable solid NH_4Cl, a black precipitate of $(NH_4)_2IrCl_6$ will be obtained while the rhodium stays in solution as red $(NH_4)_3RhCl_6$. By filtering and evaporating with concentrated NH_4OH, the rhodium is converted into yellow chloropentammine-rhodium chloride, $[RhCl(NH_3)_5]Cl_2$, somewhat soluble in hot 6 *N* HCl but precipitated as a yellow, crystalline powder on cooling. (The above procedure is excellent for detecting Rh and Ir in the presence of one another.)

4. **NH_4OH** produces (in concentrated solutions and after standing some time) a yellow precipitate of chloropentamminerhodium dichloride, $[RhCl(NH_3)_5]Cl_2$, insoluble in cold hydrochloric acid.

5. **Reducing Agents.** — Formic acid, in the presence of ammonium acetate, precipitates the black metal, as does zinc in the presence of acids. Hydroxylamine sulfate has no effect (difference from gold). Shaking with gold or mercury does not cause precipitation of metallic rhodium (difference from gold, platinum, and palladium).

Reactions in the Dry Way

All rhodium compounds are reduced to metal on being heated in a stream of hydrogen, or by heating on charcoal with sodium carbonate before the blowpipe. The metal is easily recognized by its insolubility in aqua regia, its being brought into solution by fusing with potassium pyrosulfate and then treating with water, by the formation of the brown hydroxide when KOH and a little alcohol are added to the solution thus obtained, and especially by the rose-red solution obtained by dissolving

in water the product obtained by fusion with sodium chloride in an atmosphere of chlorine gas (see p. 528).

OSMIUM, Os. At. Wt. 191.5, At. No. 76

Density 21.3–22.48. M. P. 2700°. B. P. > 5300°

Osmium and ruthenium are distinguished from the other platinum metals by their forming volatile oxides.

Properties. — Osmium, the heaviest of all metals, is compact and possesses a bluish white color very similar to zinc. It can be melted by heating in an electric furnace.* Very finely divided osmium is oxidized by the air† at ordinary temperatures, and at about 400° C it ignites and burns rapidly to OsO_4, which is volatile at 100° C. The denser the metal the higher the temperature necessary to effect the oxidation. Osmium was discovered by Tennant in 1803; its name is derived from the Greek word *osme* = odor.

Behavior toward Acids. — In the compact condition, osmium is insoluble in all acids; but in the finely divided state (as obtained by treating its zinc alloy with nitric acid), it is soluble in nitric acid, more soluble in aqua regia, and most soluble in fuming nitric acid, forming osmium tetroxide, which can be separated from the solution by distillation.

Compact osmium is brought into solution by fusing with NaOH and either KNO_3 or $KClO_3$. The melt contains a salt of perosmic acid (OsO_4).

Osmium forms five oxides:

OsO Osmious oxide, grayish black, insoluble in acids		Os_2O_3 Osmium sesquioxide, black insoluble in acids		OsO_2 Osmic oxide, black-gray, insoluble in acids
	$[OsO_3]$ Osmic acid, known only in derivatives		OsO_4 Osmium tetroxide, colorless needles soluble in water	

Osmium tetroxide, OsO_4, the most important osmium compound in the eyes of the analytical chemist, is obtained by the oxidation of the substance in the air, by dissolving the finely divided metal in fuming nitric acid or in aqua regia, or by fusing with NaOH and KNO_3 or $KClO_3$, treating the melt with nitric acid and distilling. Osmium tetroxide is a colorless, crystalline mass which sublimes at a comparatively low temperature and melts, forming colorless vapors at 100° C. The vapor has a chlorine-like odor, attacks the mucous membrane, and is poisonous.

The chlorides of osmium can be obtained only in the dry way; $OsCl_2$, $OsCl_3$, $OsCl_4$ are known. The potassium salt of the hypothetical chlorosmic acid, H_2OsCl_6, forms dark-red octahedrons, soluble in water and decomposed by boiling the solution. By heating finely divided osmium with KCl in a current of chlorine, $K_2[OsCl_6]$ is formed; it dissolves in cold water, forming a red solution.

Reactions in the Wet Way

Use a solution of $K_2[OsCl_6]$.

1. **Distillation with Acid.** — If a solution of osmium chloride or bromide is treated with dilute nitric acid, or perchloric acid, the mixture

* F. Mylius and R. Dietz, *Ber.*, **1898**, 3187.

† Cf. Ot. Sulc, *Z. anorg. Chem.*, **19**, 332.

distilled from a small retort, and the vapors received in caustic soda solution, the latter will be colored yellow, owing to the formation of $[OsO_4(OH)_2]^{=}$. If this solution is now acidified, osmium tetroxide is set free, and can be recognized by its very penetrating odor. On adding a little sodium thiosulfate to the acid solution and warming, a brown precipitate of osmium sulfide is formed.

2. **H_2S** precipitates brownish black osmium sulfide, insoluble in ammonium sulfide. The precipitate is obtained in both acid and alkaline solutions.

3. **Indigo** is decolorized by solutions containing OsO_4. Ferrous sulfate precipitates black osmium dioxide; stannous chloride produces a brown precipitate soluble in HCl, forming a brown solution.

4. **KOH, NH_4OH,** or **K_2CO_3** precipitates reddish brown osmium hydroxide, $Os(OH)_4$.

5. **Reducing Agents.** — If the solution of the chloride is treated with tannic acid and alcohol and a little hydrochloric acid is added, it is colored dark blue, owing to the formation of osmium dichloride, $OsCl_2$. KI reduces octavalent osmium to the quadrivalent state with liberation of iodine; the solution is colored a deep reddish purple.

6. **Na_2O_2.** — Fusion with Na_2O_2 converts Os into Na_2OsO_4 which dissolves in water giving an orange-yellow solution. If the solution is made acid and heated, no volatile OsO_4 escapes if the precaution is taken to add some alcohol to keep the osmium in the reduced condition; the alcohol changes the color from orange-yellow to mauve.

Reactions of Osmium Tetroxide

Osmium tetroxide melts when added to boiling water and dissolves slowly. The solution is colorless, does not react acid, but has an unpleasant odor. The fumes of OsO_4 are very poisonous and cause inflammation of the eyes.

1. **$FeSO_4$** precipitates black osmium dioxide.

2. **Indigo Solution** is decolorized.

3. **H_2S** at first colors the solution dark brown; on adding acid a dark brown precipitate of osmium tetrasulfide, OsS_4, is obtained which is insoluble in alkali hydroxide, carbonate, or sulfide.

4. **KOH** added in excess to the concentrated solution colors it yellow. If this alkaline solution is boiled, the greater part of the tetroxide distils off (very characteristic) and the remainder decomposes into oxygen and potassium osmiate, K_2OsO_4; upon long boiling osmium tetroxide, osmic hydroxide, and potassium hydroxide are formed from it.

5. **KNO_2** forms red crystals of potassium osmiate. The same compound can be obtained by reducing osmium tetroxide solution with alcohol.

6. **Potassium Iodide** reduces osmium tetroxide in acid solutions. If 2 ml of 1 per cent potassium iodide solution and 20 drops of concentrated sulfuric acid are mixed with 1 drop of osmium salt solution, a green solution of H_2OsI_4 is obtained; the colored compound can be shaken out with ether.

7. $SnCl_2$ gives a brown precipitate which dissolves in hydrochloric acid to form a brown solution.

8. SO_2 reduces osmium tetroxide. As the reduction proceeds, the color changes to yellow, reddish brown, green, and finally to indigo blue.

9. Zinc, and other metals, in the presence of acid causes precipitation of metallic osmium.

Reactions in the Dry Way

All osmium compounds are reduced to metal on being heated in a stream of hydrogen.

RUTHENIUM, Ru. At. Wt. 101.7, At. No. 44

Density 12.26, crystallized; 11.0, fused. M. P. 2450° B. P. 2700°

Properties. — Ruthenium can be obtained in the form of a dark gray or black powder, and in the form of bright porous sticks; it is brittle, can be powdered, and is melted in the oxyhydrogen flame. It was discovered by Claus in 1845 and is named after *Ruthenia* = Russia.

On being melted, a part of the ruthenium is oxidized to ruthenium tetroxide, a volatile substance having a penetrating odor similar to that of OsO_4. The molten metal spurts on cooling.

Behavior toward Acids. — Ruthenium is practically insoluble in all acids, even aqua regia. By fusing with KOH and KNO_3 (or $KClO_3$) it is oxidized to potassium ruthenate, $K_2[RuO_4]$.

On heating with KCl in a current of chlorine, soluble $K_2[RuCl_6]$ is formed. The greenish black melt dissolved in water gives an orange-yellow solution which colors the human skin black. Gradually on standing, or immediately on boiling, a black, voluminous colloidal precipitate forms (sensitive reaction). Ruthenium is unaffected by fusion with potassium pyrosulfate.

It forms the following oxides:

$$RuO,\ Ru_2O_3,\ RuO_2,\ [RuO_3],\ [Ru_2O_7],\ RuO_4$$

The most important of the oxides is RuO_4. It is formed:

(*a*) By roasting the metal itself, or its oxide, above 1000° C (osmium forms the volatile tetroxide at 400° C).

(*b*) By fusing the metal with KOH and KNO_3 in a silver crucible, dissolving the melt in water, saturating the cold solution with chlorine gas, and distilling the solution from a small retort:

$$K_2RuO_4 + Cl_2 \rightarrow 2\ KCl + RuO_4$$

(*c*) By treating the solution of potassium ruthenate with KOH and Cl, and subsequently distilling.

(*d*) By distilling potassium ruthenate with $KClO_3$ and HCl.

*By distilling a dilute solution after the addition of nitric acid, no RuO_4 will be evolved** (difference from osmium). If, however, the solution is evaporated with perchloric acid to fumes, RuO_4 is volatilized.

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* In the presence of concentrated nitric acid, however, RuO_4 is formed:

$$2\ K_2RuO_4 + 4\ HNO_3 \rightarrow 4\ KNO_3 + Ru(OH)_4 + RuO_4\ \uparrow$$

Ruthenium tetroxide forms gold-yellow, glistening, orthorhombic needles that are volatile and emit a characteristic odor; it boils at 100° C and is only slightly soluble in water. It is changed by the addition of alcohol and HCl into ruthenium trichloride, $RuCl_3$ (or sesquichloride, Ru_2Cl_6). If the solution of the latter salt is made ammoniacal, treated with sodium thiosulfate, and warmed, an intense reddish violet coloration will be produced. (This is a very sensitive and characteristic reaction.)

On treating a solution of potassium rutheniate with nitric acid, black $Ru(OH)_3$ is precipitated; it dissolves in hydrochloric acid, forming a yellow to brown solution of $RuCl_3$.

Reactions in the Wet Way

Use a solution of $RuCl_3$.

1. **H_2S** produces no precipitation at first, but after some time the solution becomes azure-blue, and brown ruthenium sulfide is precipitated (very sensitive and characteristic).

2. **Hydroxylamine** reduces ruthenium tetrachloride to ruthenium trichloride (difference from platinum).

3. **KCNS,** in the absence of other platinum metals, produces gradually a red, then a purple, and on warming a violet, coloration (very characteristic).

4. **KI** precipitates a black iodide; the reaction is aided by heating.

5. **KOH** and **NaOH** precipitate black ruthenium hydroxide, $Ru(OH)_3$, soluble in acids but insoluble in alkalies.

6. **$(NH_4)_2S$** precipitates the brownish black sulfide, difficultly soluble in an excess of the reagent.

If a ruthenium solution is made slightly alkaline with sodium carbonate and is boiled a short time with potassium nitrite, then, after cooling, a little ammonium sulfide will give a beautiful, carmine-red color which eventually turns to brown. More ammonium sulfide gives a brown precipitate. The red color is caused by $[Ru(NO_2)_6]^{--}$ anions.

7. **Zinc** at first colors the solution of the chloride azure blue, but subsequently the solution is decolorized and ruthenium itself is precipitated. Shaking with gold or mercury does not cause precipitation of metallic ruthenium (difference from gold, platinum, and palladium).

IRIDIUM, Ir. At. Wt. 193.1, At. No. 77

Density 22.4. M. P. 2350°? B. P. 4800°

Properties. — When produced by the ignition of ammonium chloriridate, $(NH_4)_2IrCl_6$, iridium is obtained in the form of a gray, spongy mass, very difficultly soluble in aqua regia. After being strongly ignited, it is almost completely insoluble in aqua regia.

The metal, although brittle, is similar to platinum. It was discovered by Tennant in 1803 and gets its name from the Latin *iris* = rainbow. Iridium is alloyed with platinum for making weights, fountain-pen points, etc.

It is more soluble in aqua regia after it has been precipitated from solutions in a very finely divided form by means of formic acid, or when it is alloyed with other metals (Au, Pt). The metal is unaffected by fusing with potassium pyrosulfate (difference from rhodium). It is oxidized by fusing with NaOH and KNO_3 in a silver crucible, but the compound formed (Ir_2O_3 combined with sodium) is only partly soluble in water. If the melt is treated with aqua regia, however, a dark red solution of $Na_2[IrCl_6]$ will be obtained.

By heating the metal with NaCl in a current of chlorine, $Na_2[IrCl_6]$ is readily obtained which forms with water a reddish brown solution.

Iridium forms the following oxides:

Ir_2O_3?	IrO_2	and the hydroxide	$Ir(OH)_4$
Bluish black	Needles with a metallic luster		Indigo-blue powder

The dark color of the chlorides is very characteristic:

$IrCl_3$*	$IrCl_4$
Dark green and brown	Black

Reactions in the Wet Way

Use a solution of $Na_2[IrCl_6]$.

1. **H_2S** at first decolorizes the solution, owing to the reduction of the tetrachloride to the trichloride, accompanied by the deposition of sulfur; subsequently brown Ir_2S_3 is precipitated, readily soluble in $(NH_4)_2S$.

Iridium is the hardest of all the platinum metals to precipitate with hydrogen sulfide. It precipitates more readily from hydrochloric acid solutions than from perchloric acid solutions.

2. **Chlorine.** — If chlorine is conducted into a dilute solution of iridium tetrachloride, the latter becomes reddish violet according to W. Palmaer;† after some time the red color disappears and the solution turns brown. The same red color has been observed by Foerster‡ at an iridium anode in sulfuric acid. According to Palmaer, the red color is due to the formation of an iridium compound having a higher valence than four.

3. **KCl** precipitates brownish black potassium chloriridate, $K_2[IrCl_6]$, insoluble in KCl and in alcohol, difficultly soluble in water.

4. **NaOH,** on being added to the solution, changes the color from dark red to green; on warming the solution it is at first colored reddish and finally azure blue:

$$2\ IrCl_4 + 2\ NaOH \rightarrow 2\ IrCl_3 + NaCl + H_2O + NaOCl$$

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* According to W. Palmaer, *Z. anorg. Chem.*, **10**, 322–326 (1895), $IrCl_3$ and its double salts exist in two modifications: dark green and brown.

† *Z. anorg Chem.*, **10**, 358 (1895).

‡ *Z Electrochem.*, **10**, 715.

If the solution is now acidified with HCl, a little alcohol* added and then some KCl, there will be no precipitation, because the $K_3[IrCl_6]$ formed is readily soluble in water and in KCl solution (difference from platinum).

If sodium hypochlorite or hypobromite is added to the alkaline solution, blue IrO_2 is formed.

5. **NH_4Cl** precipitates dark red ammonium chloriridate, $(NH_4)_2[IrCl_6]$, insoluble in a saturated solution of NH_4Cl.

If a solution of potassium or ammonium salt of H_2IrCl_6 in hot water is treated with potassium nitrite, the olive-green potassium or ammonium salt of H_3IrCl_6 is obtained:

$$K_2IrCl_6 + KNO_2 \rightarrow K_3IrCl_6 + NO_2\uparrow$$

On cooling the salt crystallizes. If, however, an excess of potassium nitrite is added to the hot green solution, it turns yellow and finally a *white* precipitate is formed.

6. **Reducing Agents** usually change the solution to a greenish color, owing to the reduction of the tetrachloride to trichloride; or the solution is decolorized and black, finely divided metal is deposited.

Thus if the solution is warmed with KNO_2, an olive-green coloration is produced:

$$IrCl_4 + KNO_2 \rightarrow IrCl_3 + KCl + NO_2\uparrow$$

If the solution is boiled for some time with an excess of KNO_2, it becomes yellow, and a part of the iridium separates out in the form of a yellowish white precipitate, difficultly soluble in cold hydrochloric acid or in boiling water. The precipitate has the following composition: $3\ K_3[Ir(NO_2)_6] \cdot K_3[IrCl_6]$.

Formic acid alone reduces iridium solutions incompletely to metal: the reduced metal is not easily dissolved by aqua regia. Shaking an iridium solution with silver or with mercury does not reduce the iridium to metal (difference from Pt, Pd, and Au).

Oxalic acid, ferrous sulfate, stannous chloride, and hydroxylamine reduce the tetrachloride to trichloride. Zinc reduces it to metal, and so does formic acid on warming in the presence of ammonium acetate. If considerable mineral acid is present the reduction takes place less readily.

Boiling with stannous chloride and adding an excess of caustic alkali gives a leather-colored precipitate.

Reactions in the Dry Way

After fusing with sodium carbonate, the gray, brittle metal can be obtained by the action of the upper reducing flame. It is insoluble in aqua regia. **Na_2O_2** fusion in a nickel crucible converts iridium into an oxide or sodium salt which is insoluble in water. The residue dissolves readily in HCl.

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* The alcohol reduces NaOCl to NaCl.

SEPARATION AND DETECTION OF THE SIX PLATINUM METALS

The separation and detection of ruthenium, rhodium, palladium, osmium, iridium, and platinum (elements 44, 45, 46, 76, 77, and 78 in the periodic table) is difficult because all these metals belong in Family VIII (cf. p. 87) and have similar properties. Moreover, the elements are rare and expensive so that it is important to be able to detect small quantities. For a long time the work of Sainte-Claire Deville, Debray, and Stas* was considered authoritative, and in the early editions of this book, reference was also made to the scheme of analysis proposed by Mylius and Dietz.† In later editions, the procedure worked out by A. A. Noyes and his students was recommended. More recently Gilchrist and Wichers,‡ working at the National Bureau of Standards, have developed a simpler procedure which is also more accurate. They were able to determine 0.015 to 0.3 g of any or all the members of this group within 0.3 mg of the truth. The following scheme of analysis is based upon this procedure of Gilchrist and Wichers without attempting, however, to give all the details and state all the precautions that are necessary for precise, quantitative analysis.

Nearly all schemes of analysis take advantage of the volatility of OsO_4 and RuO_4, elements 44 and 76 in the periodic table. Osmium tetroxide is volatilized by boiling the solution which is strongly acid with HNO_3, HNO_3 and $HClO_4$, or H_2SO_4. Noyes

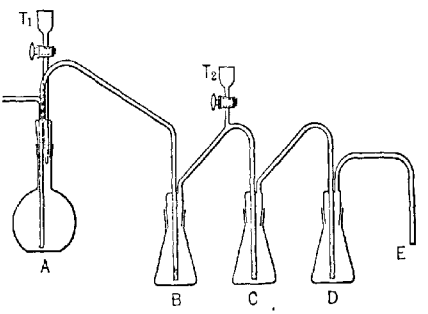


FIG. 18

recommended distilling off both the oxides from a mixture of HNO_3 and $HClO_4$, but Gilchrist and Wichers prefer to distil the OsO_4 off from a solution containing HNO_3 and after the removal of the osmium add $KBrO_3$ and then distil off the RuO_4. The following procedure is based on the method of Gilchrist and Wichers and should detect the presence of 1 mg of any constituent in the presence of as much as 0.2 g of any other. It is assumed that not over 0.3 g of all six platinum metals is present.

Distillation Apparatus. — The 700-ml flask *A* shown in Fig. 18 is provided with a ground-glass stopper with three openings, carrying (1) a tube through which air can be introduced into the flask during the distillation, (2) a dropping funnel through

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* *Procés verbaux du comité intern. des poids et mesures*, 1877-9.

† *Ber.*, **1898**, 3187.

‡ *J. Am. Chem. Soc.*, **57**, 2565 (1935).

which solution can be introduced into the flask, and (3) an exit tube which provides connection with the three 300-ml Erlenmeyer flasks, *B*, *C*, and *D*. Each of these three flasks is provided with a ground-glass stopper so that the gas evolved from flask *A* does not come in contact with rubber or even stopcock lubricant because if OsO_4 comes in contact with organic matter it is likely to be decomposed with deposition of OsO_2. The joints are sealed with a film of water. Between the receivers *B* and *C*, the gas delivery tubing is connected with a dropping funnel T_2 through which $NaHCO_3$ solution can be added when necessary. The only part of the apparatus that is greased is the stopcock below the dropping funnel T_1. During the distillation it is well occasionally to flush out with water the tubing below T_1 to remove any OsO_4 which may have diffused into it.

1. **Removal of Osmium as OsO_4.** — In the flask *B*, place 150 ml of 6 *N* HCl that has been freshly saturated with SO_2 and add 50-ml portions of the same solution to each of the flasks *C* and *D*. For qualitative tests only one absorbing flask is necessary. Transfer the solution to be tested to the distilling flask *A* and dilute, if necessary, to about 100 ml. Through T_1 add 40 ml of 7.5 *N* HNO_3. Flush the funnel and tubing with 10 ml of water. Pass a slow stream of air through the apparatus by applying gentle suction at *E*. Heat the solution in *A* to boiling, and continue boiling for an hour. (If the osmium is present as $OsCl_6^{--}$ salt the distillation will require seven to eight hours to eliminate all the osmium from a solution containing 0.3 g of the metal. In that case it is preferable to use concentrated H_2SO_4 and a little HNO_3 in place of the 40 ml of HNO_3 prescribed above. This will greatly reduce the time required.) Practically all the osmium will be absorbed in the first receiver, *B*. The solution that remains in the distilling flask will contain only Ru, Pt, Pd, Rh, and Ir. (See 3.)

2. **Detection of Osmium.** — For qualitative purposes, it can be assumed that only the contents of the receiver *B* need be tested. Transfer the solution to a beaker, and evaporate nearly to dryness on the steam-bath. To the residue add 10 ml of 12 *N* HCl and digest for fifteen minutes on the bath. Divide the resulting solution into three portions, and apply the following three tests:

(*a*) Dilute one portion to about 100 ml and saturate with H_2S; a dark brown sulfide precipitate indicates the presence of Os.

(*b*) Evaporate off most of the acid from another portion, dilute with a little water and add some solid thiourea; a deep rose color develops if Os is present. This test is sensitive.

(*c*) Evaporate the third portion just to dryness. Dissolve in 50 ml of water, heat to boiling and neutralize with 10 per cent $NaHCO_3$ solution until a precipitate forms or the solution is alkaline to bromophenol blue, which turns from yellow to blue at p_H 4. The formation of a reddish brown precipitate of hydrated OsO_2 indicates the presence of Os.

3. **Removal of Ruthenium as RuO_4.** — Transfer the solution remaining in flask *A*, after the treatment described in (1), to a beaker or evaporating dish, and evaporate to dryness on the steam-bath. Add 10 ml of 12 *N* HCl and again evaporate. Repeat this treatment until oxides of nitrogen are no longer evolved. Dissolve the last residue in 20 ml of water and evaporate carefully until heavy fumes of sulfuric acid are evolved. Cool, carefully add 10 ml of water, dropwise at first, and return the sulfuric acid solution to the same flask, *A*, that was used for the removal of osmium. If any platinum has been deposited in the beaker, wash this also into the flask. Dilute the solution to 100 ml, add 100 ml of 10 per cent $KBrO_3$ solution, and distil as described under (1) with fresh portions of HCl–SO_2 in the three receivers. After

distilling about 90 minutes, by boiling gently and passing a current of air through the solution, add 25 ml more of the bromate solution and distil another hour. During the distillation it is best to add occasionally a little saturated, aqueous SO_2 solution through the funnel T_2, which is between the first and second absorption flasks. This keeps an excess of SO_2 in the absorbent. After the 2.5 hours of distilling, it can be assumed that all ruthenium has been distilled off as RuO_4. Preserve the solution in the flask for the Pt, Pd, Rh, and Ir tests. (See 5.)

4. **Detection of Ruthenium.** — Transfer the contents of the receiver *B*, which can be assumed to contain most of the ruthenium, to a beaker, and evaporate to a moist residue on the steam-bath. Add 10 ml of 12 *N* HCl, and digest on the steam-bath with the beaker covered for an hour. Add 50 ml of water, and heat to boiling to dissolve the residual ruthenium compound. Divide the solution into three portions, and apply the following tests:

(*a*) Make the solution ammoniacal and add some $Na_2S_2O_3$ solution; a reddish violet coloration shows the presence of Ru.

(*b*) To the solution add some solid thiourea; a greenish or bluish color indicates Ru.

(*c*) Dilute the solution to 200 ml, heat to boiling, and carefully neutralize with 10 per cent $NaHCO_3$ solution until the solution is basic to bromocresol purple. The indicator changes from yellow to blue at p_H about 6. If Ru is present a dark colored precipitate of hydrated Ru_2O_3 will form.

5. **Removal of Palladium, Rhodium, and Iridium as Hydrated Dioxides.** — Transfer the contents of flask *A*, after the treatment described in (3), to a liter beaker, and cautiously decompose the residual bromate by adding 12 *N* HCl. Evaporate the solution, and, when the volume is small, make sure that all bromate is decomposed by adding more HCl. (Sometimes flask *A* will be stained with IrO_2. This can be dissolved in a little aqua regia, but the solution must not be added to the main solution until nitroso compounds have been destroyed by evaporating twice with concentrated HCl.) Finally evaporate as far as possible on the steam-bath. Dilute with water to 200 ml.

If the solution at the start was known to contain no osmium or ruthenium, the treatment described under (1), (2), (3), (4), and the above paragraph should be omitted. In such cases, evaporate the solution with HCl to a moist residue on the steam-bath and repeat the evaporation with HCl if any nitric acid has been used in preparing the solution. Finally add 2 g of NaCl and 5 ml of 12 *N* HCl and evaporate to dryness. To the residue add 2 ml of 12 *N* HCl and dilute to 200 ml.

Heat the solution containing Pt, Pd, Rh, and Ir to boiling and add 20 ml of 10 per cent $NaBrO_3$ solution. Carefully add 10 per cent $NaHCO_3$ solution until the dark green solution shows evidence of the formation of a permanent precipitate. At p_H 6, all the Rh and Ir and most of the Pd will precipitate as hydrated dioxides. At p_H 6, bromocresol purple indicator changes from yellow to blue. Test the boiling hot solution from time to time as follows: Place a stirring-rod in the solution and remove it. Allow a drop of 0.01 per cent bromocresol purple solution to run down the stirring-rod into the drop of solution which is clinging to the bottom of the rod. Enough $NaHCO_3$ has been added when the drop at the end of the stirring-rod causes the indicator to change from yellow to blue. Now add 10 ml more of the 10 per cent bromate solution and boil five minutes. Increase the p_H to 10 by adding the $NaHCO_3$ solution dropwise until a drop of the solution, tested as described for the other indicator, shows a pink color with a drop of 0.01 per cent cresol red indicator. Then add a final portion of 10 ml of 10 per cent $NaBrO_3$ solution and boil fifteen

minutes. Filter, and use the filtrate for the platinum test; the precipitate is hydrated PdO_2, RhO_2, and IrO_2. Wash the precipitate with 1 per cent NaCl solution. Examine it as described under (7).

6. **Detection of Platinum.** — Carefully add HCl to the filtrate until all $NaHCO_3$ is decomposed. Then add 20 ml of concentrated HCl and evaporate to dryness. Add 10 ml more of 12 *N* HCl and again evaporate to dryness to make sure that all bromate is decomposed. Add 5 ml of 12 *N* HCl warm, dilute to about 100 ml, and filter. Divide the solution into three parts, and test for platinum by reactions 1, 3 and 6 on page 522.

7. **Detection of Palladium.** — Dissolve the precipitated oxides of palladium, rhodium, and iridium by heating with 20 ml of concentrated HCl on the steam-bath. Dilute somewhat, filter, and dilute the filtrate to about 400 ml. Add a 1 per cent solution of dimethylglyoxime in 95 per cent alcohol in slight excess (0.22 ml of reagent should be used for each milligram of Pd present). After an hour, filter off the precipitate and wash it with hot water. The yellow precipitate is $Pd(C_8H_{14}N_4O_4)$ and contains 31.68 per cent Pd. Further identification is unnecessary.

8. **Detection of Rhodium.** — To the filtrate from the palladium precipitate, add 10 ml of concentrated sulfuric acid and evaporate to fumes of H_2SO_4. The excess of dimethylglyoxime reagent will cause charring at this stage. Cool, add about 2 ml of concentrated nitric acid, and heat till dense fumes are evolved again. Continue this treatment until no more charring results. Then evaporate to fumes again, cool, add cautiously 20 ml of cold water, and again evaporate to fumes in order to make sure that all HNO_3 is evolved. Finally cool, add water dropwise until the acid has been mixed with an equal volume of water, and then dilute to about 200 ml. Heat to boiling, and add dropwise a 20 per cent solution of $TiCl_3$ to precipitate Rh. When an excess of $TiCl_3$ is present, the supernatant liquid will appear slightly purple. If much iridium is present the end point can be determined by the fact that no further precipitation takes place and the solution is orange. Boil two minutes, filter, and wash with 2.5 per cent sulfuric acid. Use the filtrate for the iridium test.

If it is thought necessary to confirm the presence of rhodium in a small precipitate, digest the paper and precipitate with sulfuric and nitric acid as just described for the removal of the excess dimethylglyoxime reagent. After there is no more charring with hot, concentrated H_2SO_4, cool, dilute with 20 ml of water, and again evaporate to fumes. Cool and repeat the treatment with $TiCl_3$.

9. **Detection of Iridium.** — Cool the filtrate from the rhodium precipitation by placing the beaker in crushed ice. Add a chilled, freshly prepared, 6 per cent solution of cupferron in slight excess, to precipitate the excess of titanium. Filter and wash with 2.5 per cent H_2SO_4. Evaporate the filtrate to dryness, and destroy the excess of cupferron by treatment with HNO_3 as described under (8). Further addition of H_2SO_4 is unnecessary. After the removal of the organic matter, which is likely to interfere with the hydrolytic preicpitation of any oxide of this group, neutralize the solution and precipitate hydrated IrO_2 with $NaHCO_3$ and $NaBrO_3$ exactly as described under (6). The formation of a precipitate at this point is sufficient indication of the presence of iridium.

METALS OF THE $(NH_4)_2S$ GROUP

BERYLLIUM, URANIUM, TITANIUM, ZIRCONIUM, THORIUM, YTTRIUM, ERBIUM, CERIUM, LANTHANUM, NEODYMIUM, PRASEODYMIUM THALLIUM, INDIUM, GALLIUM, OTHER RARE-EARTH ELEMENTS AND VANADIUM

BERYLLIUM, Be. At. Wt. 9.02, At. No. 4

Density 1.84. M. P. 1370°

Occurrence. – Chrysoberyl, $Be(AlO_2)_2$; phenacite, Be_2SiO_4; beryl, $Be_3Al_2Si_6O_{18}$; euclase, $AlBeHSiO_5$; meliphanite, $Be_2Ca_2NaSi_3O_{10}F$; and leucophanite, $BeCaNaSi_2O_6F$.

Properties. — Beryllium is a bivalent metal, and forms a white oxide, BeO, which is soluble in acids. The metal is stable in the atmosphere, does not decompose water, but dissolves in dilute hydrochloric and sulfuric acids and in sodium or potassium hydroxide with evolution of hydrogen:

$$Be + 2\,H^+ \rightarrow Be^{++} + H_2\uparrow, \quad 2\,Be + 4\,OH^- \rightarrow 2\,BeO_2^{--} + 2\,H_2\uparrow$$

Beryllium, like aluminum, is easily made passive by nitric acid.

The metal was discovered by Vauquelin in 1797 and isolated by Wöhler in 1828. It has an electrical conductivity exceeding that of copper and is almost as hard as quartz. Its name comes from the Greek *berullos*, a word of uncertain origin, applied to the mineral beryl and probably to other gems. Sometimes the metal beryllium is used in place of aluminum as a window in x-ray tubes. Some of its alloys have been studied, and the addition of BeO to glass instead of CaO is said to increase the hardness and raise the melting point, but the present price of $25–$30 per ton of ore with about 10 per cent of $Be_3Al_2(SiO_3)_6$ has prevented its use industrially.

The oxide BeO is said to be as good as MgO for refractory purposes, and the hydroxide, $Be(OH)_2$, resembles $Al(OH)_3$ in appearance and in its amphoteric properties. Like $Al(OH)_3$ it is slow to dissolve in acids after the precipitate has stood for some time.

Beryllium closely resembles aluminum in its chemical behavior. Beryllium salts react acid in aqueous solution and possess a sweetish, astringent taste. The element has been called glucinum, Gl.

Reactions in the Wet Way

Use a solution of $BeSO_4 \cdot 4\,H_2O$.

1. **Alkali Carbonates** give white precipitates of variable composition; usually a basic carbonate is formed. When freshly precipitated the carbonate dissolves in a large excess of sodium or potassium carbonate but is much more soluble in ammonium carbonate. By boiling the ammonium carbonate solution, reprecipitation takes place, but not

by boiling the sodium or potassium carbonate solution unless it is very dilute.

2. **Ammonia** and **Ammonium Sulfide** produce a white precipitate of $Be(OH)_2$, similar in appearance to $Al(OH)_3$, insoluble in an excess of the precipitant, but readily soluble in HCl, forming a colorless solution. The yellow color often obtained in dissolving the hydroxide in hydrochloric acid is due to traces of ferric chloride.

3. **Ammonium Carbonate** produces a white precipitate of beryllium carbonate, readily soluble in an excess of the reagent (difference from aluminum); by boiling the solution, the beryllium is precipitated as white basic carbonate. This property is used in separating beryllium from iron and aluminum. The separation is not sharp, however, which can also be said of the separation by means of caustic potash.

According to Fresenius, it is necessary to heat the solution somewhat. In order to make a quantitative separation, the beryllium hydroxide or carbonate must be redissolved and the precipitation repeated several times.

According to Parsons and Barnes* a good method of separating beryllium from aluminum consists in boiling in 10 per cent sodium bicarbonate solution; aluminum hydroxide is precipitated and beryllium remains in solution.

4. $BaCO_3$ precipitates beryllium as hydroxide.

5. **Chloroform.** — To separate beryllium from aluminum ions, Haber and Van Oordt† take advantage of the fact that $BeO \cdot 3\ Be(C_2H_3O_2)_2$ is soluble in chloroform. The hydroxides of these elements, when freshly precipitated, are dissolved in glacial acetic acid and evaporated with a little water, and the residue is extracted with chloroform.

To detect small quantities of beryllium in the presence of considerable aluminum, Rössler‡ proceeds as follows:

Dissolve the hydroxides in hydrochloric acid, evaporate to dryness, and dissolve the residue in a little water, adding a little hydrochloric acid if necessary. Rinse the solution into a heavy glass tube sealed at one end; add about twelve times as much potassium sulfate as there was aluminum and enough water to dissolve the salt on warming. Seal the tube and heat at 180° for half an hour. After cooling, open the tube, filter off the basic potassium aluminum sulfate, and precipitate the beryllium with ammonium hydroxide. To purify the beryllium hydroxide, dissolve it promptly in hydrochloric acid, add a little citric acid, and throw down the beryllium as beryllium ammonium phosphate from the boiling solution.

6. **Diammonium Phosphate** gives a gelatinous precipitate of phosphate which dissolves in a considerable excess of the reagent. By care-

* *Z. anal. Chem.*, **46**, 292.
† *Z. anal. Chem.*, **40**, 465.
‡ *Z. anorg. Chem.*, **13**, 435.

fully adding ammonia, but avoiding an excess, a crystalline precipitate of beryllium ammonium phosphate forms on boiling. Citric acid does not prevent the precipitation, as it does with aluminum, but if considerable aluminum is present, it tends to keep the beryllium in solution.

7. **Ether and HCl.** — $BeCl_2$ is soluble in a mixture of equal volumes of saturated aqueous and ethereal hydrochloric acid, while the hydrous aluminum chloride is not (good method for separating Be and Al).*

8. **KOH** precipitates white, gelatinous beryllium hydroxide, readily soluble in an excess of the reagent, forming potassium beryllate:

$$Be^{++} + 2\,OH^- \rightarrow Be(OH)_2,\ Be(OH)_2 + 2\,OH^- \rightarrow [BeO_2]^{--} + 2\,H_2O$$

The alkali beryllates are decomposed hydrolytically on boiling their dilute aqueous solutions, all the beryllium being precipitated as hydroxide. The precipitate thus obtained is denser than that thrown down by ammonia, and differs from the latter by being insoluble in potassium carbonate and difficultly soluble in ammonium carbonate solutions; it is also much more difficultly soluble in dilute acids. A solution containing a considerable excess of alkali hydroxide does not give a precipitate of beryllium hydroxide by boiling.

Tartaric acid prevents the precipitation of beryllium hydroxide.

9. **K_2SO_4** gives with beryllium sulfate a beautifully crystalline double salt, $K_2Be(SO_4)_2 \cdot 2\,H_2O$, which is soluble in a concentrated solution of K_2SO_4 (difference from Ce, La, and Di).

10. **Morin** gives no fluorescence with beryllium salt solutions.

11. **Oxalic Acid** and **Ammonium Oxalate** cause no precipitation (difference from thorium, zirconium, erbium, yttrium, cerium, lanthanum, and didymium).

12. **Sodium Thiosulfate** gives no precipitate.

Reactions in the Dry Way

Beryllium salts moistened with cobalt nitrate solution and heated give a gray mass. Fused with twice as much potassium acid fluoride, KHF_2, the mass dissolves in water containing hydrofluoric acid; under the same conditions, potassium aluminum fluoride remains insoluble.

URANIUM, U. At. Wt. 238.07, At. No. 92

Density 18.7. M. P. below 1850°

Occurrence. — The principal minerals containing uranium are pitchblende, U_3O_8; carnotite, $K_2(UO_2)_2(VO_4)_2\ 8\,H_2O$; and autunite, $(CaUO_2)_2(PO_4)_2 \cdot 8\,H_2O$. It is also found in the rarer minerals uranite, $(UO_2)_2Cu(PO_4)_2 \cdot 8\,H_2O$; samarskite (a columbite of iron, yttrium, cerium, and erbium which contains varying quantities of uranium); and liebigite, $U(CO_3)_2 \cdot 2\,CaCO_3 \cdot 10\,H_2O$.

* F. S. Havens, *Z. anorg. Chem.*, **18**, 147 (1898).

History. — The element derives its name from the planet *Uranus*. Klaproth is credited with its discovery in 1789, although, as Péligot showed in 1842, he mistook the oxide for the element itself. Péligot obtained the metal by reducing uranium tetrachloride with sodium. Since the discovery of radium, enormous quantities of uranium minerals have been worked for the radium content and uranium salts have become by-products. Uranyl nitrate, $UO_2(NO_3)_2 \cdot 6\,H_2O$, is the most important salt, and uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2\,H_2O$, ranks next. In 1929, about 136 tons of uranium oxide and salts were imported into the United States at a valuation of nearly $350,000.

Properties. — Metallic uranium resembles nickel in appearance. It is ductile and malleable; it will take a high polish, but tarnishes quickly in a moist atmosphere. Like iron, it takes fire when in the form of powder and will burn briskly when heated to 170°. Uranium decomposes water slowly at room temperature and fairly rapidly if the water is boiling. Uranium is the heaviest element, and in the periodic classification it is in the same family with oxygen, sulfur, and chromium. In the case of sulfur and chromium, we find that the element has the tendency to unite with four atoms of oxygen and form bivalent sulfate and chromate anions. Corresponding to the general rule that an element is more likely to form bases the lower it is in the family, we find that uranium, when it has the valence of +6, unites with two atoms of oxygen and forms bivalent UO_2^{++} cations, which behave in many respects like magnesium ions. Thus they form a precipitate of $UO_2NH_4PO_4 \cdot 6\,H_2O$ corresponding to $MgNH_4PO_4 \cdot 6\,H_2O$ which yields $(UO_2)_2\,P_2O_7$ upon ignition corresponding to $Mg_2P_2O_7$. Uranium with a valence of +6 also resembles chromium by forming bivalent diuranate ions, $U_2O_7^{--}$. Uranium oxides are used in ceramics for making yellow and fluorescent glass and glazes. It has been used in steel making as a substitute for tungsten in alloy steel, but there has been little demand for this product, possibly because of the cost.

Oxides and Hydroxides. — Five oxides of uranium are mentioned in the literature: UO_2, U_2O_5, UO_3, U_3O_8, and UO_4. Of these UO_2, UO_3, and U_3O_8 are definitely known although the last one may be a mixture of UO_2 and 2 UO_3. The dark brown dioxide, UO_2, is obtained when uranium burns in the air at 150–170° or when U_3O_8 is heated in hydrogen at about 625–650°. Uranium trioxide, UO_3, which is brick red in color, is formed when ammonium uranate, $(NH_4)_2U_2O_7$, or ammonium uranyl carbonate, $(NH_4)_4UO_2(CO_3)_3$, is heated not above 300°. This oxide, like WO_3 and MoO_3, is somewhat amphoteric, but its acid properties are less pronounced. It forms two hydrates: the yellow monohydrate, $UO_3 \cdot H_2O$, and the dihydrate, $UO_3 \cdot 2\,H_2O$. The former can act as uranic acid, H_2UO_4, and the latter as uranyl hydroxide, $UO_2(OH)_2$, which reacts as a base.

Out of contact with the air, uranium dioxide dissolves in strong acids, forming *uranous* salts:

$$UO_2 + 4\,HCl \rightarrow 2\,H_2O + UCl_4, \quad UO_2 + 2\,H_2SO_4 \rightarrow 2\,H_2O + U(SO_4)_2$$

The uranous salts are extremely unstable, and on being exposed to the air change rapidly, forming *uranyl* salts which contain the bivalent UO_2 group:

$$2\,UCl_4 + O_2 + 2\,H_2O \rightarrow 2\,UO_2Cl_2 + 4\,HCl$$

$$2\,U(SO_4)_2 + O_2 + 2\,H_2O \rightarrow 2\,UO_2SO_4 + 2\,H_2SO_4$$

Uranium trioxide dissolves in acids, forming uranyl salts:

$$UO_3 + 2\,HCl \rightarrow UO_2Cl_2 + H_2O$$

By igniting the oxides of uranium in air, dark-green urano-uranic oxide, U_3O_8 or $(2\ UO_3 \cdot UO_2)$, is obtained, which out of contact with the air dissolves in strong acids, forming a mixture of uranous and uranyl salts:

$$(2\ UO_3 \cdot UO_2) + 4\ H_2SO_4 \rightarrow 2\ UO_2SO_4 + U(SO_4)_2 + 4\ H_2O$$

By dissolving in aqua regia, uranyl chloride is obtained:

$$3\ U_3O_8 + 18\ HCl + 2\ HNO_3 \rightarrow 9\ UO_2Cl_2 + 2\ NO + 10\ H_2O$$

Only the reactions of uranyl salts will be described.

Uranyl compounds are colored yellow or yellowish green. Most of them are soluble in water, but the oxides, the sulfide, phosphate, and uranates are insoluble. In mineral acids most uranium compounds are soluble, with the exception of the ferrocyanide.

Beryllium behaves like uranium in the analytical scheme, but the acetate obtained by evaporating an acetic acid solution of uranyl acetate is insoluble in anhydrous chloroform, whereas basic beryllium acetate is soluble in chloroform.

Reactions in the Wet Way

1. **Alkali Hydroxide** precipitates yellow amorphous potassium uranate. Uranyl hydroxide, $UO_2(OH)_2$, is first formed and changes into an insoluble alkali salt of uranic acid, $H_2U_2O_7$:

$$2\ UO_2Cl_2 + 6\ KOH \rightarrow \mathbf{K_2U_2O_7} + 4\ KCl + 3\ H_2O$$

2. **Ammonia** precipitates yellow, amorphous ammonium uranate:

$$2\ UO_2(NO_3)_2 + 6\ NH_4OH \rightarrow \mathbf{(NH_4)_2U_2O_7} + 4\ NH_4NO_3 + 3\ H_2O$$

The alkali uranates are soluble in alkali carbonates, particularly in ammonium carbonate, with the formation of complex salts:

$$\mathbf{(NH_4)_2U_2O_7} + 6\ (NH_4)_2CO_3 + 3\ H_2O \rightarrow 2\ (NH_4)_4[UO_2(CO_3)_3] + 6\ NH_4OH$$

Consequently, in the presence of sufficient alkali carbonate, ammonia fails to precipitate uranium. Tartaric and citric acids (and other organic substances) also prevent the precipitation with ammonia and caustic alkalies, as with iron, chromium, and aluminum, whereas tannin gives a dark brown precipitate in the tartrate solution containing acetate.

3. **Ammonium Sulfide** precipitates brown uranyl sulfide,

$$UO_2(NO_3)_2 + (NH_4)_2S \rightarrow 2\ NH_4NO_3 + \mathbf{UO_2S}$$

soluble in dilute acids and in ammonium carbonate:

$$\mathbf{UO_2S} + 3\ (NH_4)_2CO_3 \rightarrow (NH_4)_2S + (NH_4)_4[UO_2(CO_3)_3]$$

Ammonium sulfide, therefore, produces no precipitate in solutions of uranyl salts in the presence of ammonium carbonate.

By boiling the solution of uranium salt to which ammonium sulfide has been added, the uranyl sulfide decomposes into sulfur and black uranous oxide, UO_2, which is insoluble in an excess of the ammonium sulfide and in ammonium carbonate solution. If uranyl sulfide stands for some time in contact with an excess of am-

monium sulfide, it is gradually changed into a red substance with access of air or to a black substance if air is excluded; the reaction is probably due to the formation of ammonium thiosulfate.

4. **Barium Carbonate** precipitates in the cold all the uranium, probably as barium uranyl carbonate:

$$UO_2(NO_3)_2 + 3\ BaCO_3 \rightarrow Ba(NO_3)_2 + \mathbf{Ba_2[UO_2(CO_3)_3]}$$

5. **Hydrogen Peroxide** precipitates yellowish uranium tetroxide, insoluble in hydrochloric acid. The presence of sulfate ions hinders the precipitation. The oxide dissolves in ammonium carbonate solution, giving a deep yellow solution. If the precipitate produced by hydrogen peroxide is dissolved in sulfuric acid and the solution is shaken with a little ether, the ether is colored blue.

6. **Mercuric Oxide** suspension precipitates uranium completely by boiling the solution containing ammonium chloride. (Separation of uranium from strontium, calcium, and alkali ions and less satisfactorily from barium ions.)

7. **Potassium Ferrocyanide** produces a brown precipitate, or in very dilute solutions, a brownish red coloration:

$$Fe(CN)_6^{=\,=} + 2\ UO_2^{++} \rightarrow \mathbf{(UO_2)_2[Fe(CN)_6]}$$

On addition of potassium hydroxide the brownish red precipitate becomes yellow, owing to the formation of potassium uranate:

$$\mathbf{(UO_2)_2[Fe(CN)_6]} + 6\ KOH \rightarrow K_4[Fe(CN)_6] + 3\ H_2O + \mathbf{K_2U_2O_7}$$

(This effect and the fact that the precipitate of ferrocyanide does not form in dilute acetic acid solutions serves to prevent interference of uranium with the test for copper.)

The ferrocyanide test for UO_2^{++} is very sensitive and succeeds with less than 1 γ of uranium. The test can be made in the presence of iron and copper if KI is added to reduce the iron to the ferrous and the copper to the cuprous state. Then, after adding sodium thiosulfate solution to react with the liberated iodine, the test for uranium appears. When both copper and iron are present, the reduction succeeds with thiosulfate alone; the copper acts as a catalyzer.

8. **Sodium Carbonate** produces in concentrated solutions an orange-yellow precipitate of sodium uranyl carbonate:

$$UO_2(NO_3)_2 + 3\ Na_2CO_3 \rightarrow 2\ NaNO_3 + \mathbf{Na_4[UO_2(CO_3)_3]}$$

Sodium uranyl carbonate is soluble in *considerable* water, so that no precipitate is formed from dilute solutions. It is still more soluble in alkali carbonate solution, particularly in a bicarbonate solution. From

such solutions sodium hydroxide precipitates sodium uranate, but ammonia produces no precipitation.

9. **Sodium Peroxide** produces a yellow precipitate soluble in an excess of the reagent; the addition of alcohol then precipitates yellow sodium peruranate, $Na_2UO_5 \cdot 5\,H_2O$.

10. **Sodium Phosphate** precipitates yellowish white uranyl phosphate,

$$UO_2(NO_3)_2 + Na_2HPO_4 \rightarrow 2\,NaNO_3 + \mathbf{UO_2HPO_4}$$

while, in the presence of ammonium acetate, uranyl ammonium phosphate is precipitated:

$$Na_2HPO_4 + UO_2(NO_3)_2 + NH_4C_2H_3O_2 \rightarrow$$
$$2\,NaNO_3 + HC_2H_3O_2 + \mathbf{UO_2NH_4PO_4}$$

Both precipitates are insoluble in acetic acid, but soluble in mineral acids.

11. **Turmeric Paper** is colored brown by aqueous solutions of uranyl salts, especially the nitrate. The presence of considerable acid prevents the reaction.

12. **Zinc,** in the presence of dilute sulfuric acid, reduces yellow uranyl salt to green uranous salt.

Reactions in the Dry Way

The borax (or sodium metaphosphate) bead is yellow in the oxidizing flame and green in the reducing flame.

TITANIUM, Ti. At. Wt. 47.90, At. No. 22

Density 4.49. M. P. 1795° ± 5°. B. P. > 3000°

Occurrence. — Titanium occurs in nature most frequently as the dioxide: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) Titanium is also found in the minerals perowskite, $CaTiO_3$; titanite, $CaSiTiO_5$; and ilmenite, $FeTiO_3$; as well as in many crystalline rocks. It is present in most rocks, but usually only in very small quantity.

Properties. — Titanium itself is a gray metal, very similar to iron. Its name is derived from *Titans*, the giants of Greek mythology. On being heated in the air it burns brightly to white titanium dioxide, and it also unites with nitrogen to form a nitride. The metal is hard enough to scratch glass; it is very brittle when cold but can be forged and drawn into wire at a red heat. In its chemical properties it resembles cerium, thorium, zirconium, and hafnium. There is no demand for titanium metal, but ferro-titanium has been used in steel making as a "scavenger," and copper-titanium or manganese-titanium (alloys with 10 to 30 per cent titanium) are used similarly in making bronze castings. Enormous quantities of titanium dioxide are now used in making white paints; the pigment has good covering power and is stable toward atmospheric gases.

Oxides. — Four oxides of titanium have been described. Titanium monoxide, TiO or Ti_2O_2, has been made by reducing TiO_2 with carbon or magnesium at a high

temperature. It is basic, but its salts are of no importance because of their instability. Titanium trioxide, Ti_2O_3, or sesquioxide as it was formerly called, is formed as black, lustrous crystals by heating TiO_2 in hydrogen. Its salts are violet or green in color and are energetic reducing agents; titanous chloride, $TiCl_3$, is comparable to stannous chloride, $SnCl_2$, as a reducing agent and is used for titrating ferric salts in quantitative analysis. The precipitate, $Ti(OH)_3$, formed on adding alkali hydroxide or ammonia to a solution of a titanous salt, is dark colored and very unstable. Titanium dioxide is the most important oxide and represents titanium's most stable state of oxidation. The hydroxide, $Ti(OH)_4$ or $TiO(OH)_2$, is somewhat amphoteric, but it is more basic than acidic; even the alkali salts are insoluble in water because they are hydrolyzed. The hydroxide is oftener called metatitanic acid, H_2TiO_3, than titanic hydroxide. Titanium dioxide as it occurs in nature (rutile, etc.) is insoluble in all acids. In order to bring it into solution it is best to fuse it with potassium pyrosulfate, whereby it is changed into titanium sulfate:

$$TiO_2 + 2\ K_2S_2O_7 \rightarrow Ti(SO_4)_2 + 2\ K_2SO_4$$

The cold melt is soluble in *cold* water. The oxide can also be dissolved by fusing with sodium carbonate and treating the product with 6 *N* hydrochloric acid. Titanium peroxide is formed when an acid solution of titanium salt is treated with hydrogen peroxide. The formulas TiO_3, $TiO_2 \cdot H_2O_2$, and H_4TiO_5 have been proposed for titanium peroxide; it has also been called *peroxytitanic acid*. The formula

$$H_2\left[Ti\begin{matrix}O\\ \|\\ O\end{matrix}(SO_4)_2\right]$$

is favored for the compound produced on adding H_2O_2 to titanium sulfate solution.

Solubilities. — Metallic titanium is readily soluble in hydrofluoric acid. The tetrafluoride, TiF_4, boils at 284° and unites with excess hydrofluoric acid to form the complex fluortitanic acid, H_2TiF_6, which has a difficultly soluble potassium salt, K_2TiF_6. In quantitative analysis, the chemist often has to deal with a precipitate of hydrated silicic acid containing some hydrated TiO_2. The SiO_2 content of the precipitate is determined by igniting to constant weight, heating with sulfuric and hydrofluoric acids, heating again, and weighing the residue. The first weight corresponds to $SiO_2 + TiO_2$. By the treatment with HF, SiF_4 and possibly TiF_4 are formed. On heating in the presence of H_2SO_4, all the SiF_4 is volatilized as such, but, before any TiF_4 escapes, it is changed to $Ti(SO_4)_2$ which on further heating loses SO_3 and the residue after the final heating is TiO_2.

Titanium dissolves in hot dilute hydrochloric acid and $TiCl_3$ is formed if the solution is protected from oxidation. Dilute nitric acid forms H_2TiO_3 slowly, and concentrated nitric acid forms it rapidly; the H_2TiO_3 is only slightly soluble. Aqua regia attacks the metal, but a coating of H_2TiO_3 soon protects it. Cold, dilute sulfuric acid dissolves titanium to form $Ti_2(SO_4)_3$ and hydrogen; but hot concentrated sulfuric acid forms $Ti(SO_4)_2$ and SO_2. Titanic hydroxide, $Ti(OH)_4$ or $TiO(OH)_2$, *when freshly precipitated from cold solutions*, is easily dissolved by dilute mineral acids or by alkali carbonate or ammonium carbonate, but after the precipitate has stood for some time, or has been heated, it becomes insoluble in dilute acids and is not dissolved appreciably by boiling with caustic alkalies or alkali carbonates. It is dissolved slowly by heating with concentrated sulfuric acid. The sulfate, $Ti(SO_4)_2$, is soluble in cold, dilute sulfuric acid but in the absence of sufficient acid is easily hydrolyzed to insoluble basic titanyl sulfate, $TiO \cdot SO_3$ or to H_2TiO_3 ($TiO(OH)_2$). Titanium tetrachloride, $TiCl_4$, is a liquid which boils at 136°. It,

as also the tetraiodide, TiI_4, has been used for the production of metallic titanium; the halogen compounds are reduced by heating with sodium or sodium hydride. The salts of quadrivalent titanium are colorless.

Reactions in the Wet Way

For these reactions a solution of titanium sulfate or of titanium hydroxide in hydrochloric acid can be used.

1. **Alkali Hydroxide** precipitates, in the cold, gelatinous *orthotitanic* acid,

$$Ti^{++++} + 4\ OH^- \rightarrow \mathbf{H_4TiO_4}$$

which is almost insoluble in an excess of the reagent, but readily soluble in mineral acids.

If the precipitation by potassium hydroxide takes place from a hot solution the titanium is precipitated as *metatitanic* acid,

$$Ti^{++++} + 4\ OH^- \rightarrow H_2O + \mathbf{H_2TiO_3}$$

which is difficultly soluble in dilute acids. By long digestion with concentrated hydrochloric or sulfuric acid it goes gradually into solution. By the ignition of both these titanic acids the anhydride TiO_2 is obtained, which is only slightly soluble in concentrated hydrochloric acid, but readily soluble in hot concentrated sulfuric acid.

2. **Alkali Acetates** on boiling precipitate all the titanium as metatitanic acid:

$$Ti^{++++} + 4\ C_2H_3O_2^- + 3\ H_2O \rightarrow 4\ HC_2H_3O_2 + \mathbf{H_2TiO_3}$$

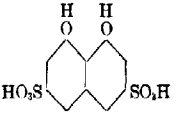
3. **Ammonia, Ammonium Sulfide,** and **Barium Carbonate** (like potassium hydroxide) precipitate, in the cold, orthotitanic acid, readily soluble in acids; and from hot solutions the difficultly soluble metatitanic acid:

$$TiCl_4 + 4\ NH_4OH \rightarrow 4\ NH_4Cl + \mathbf{H_4TiO_4}$$

$$TiCl_4 + 2\ (NH_4)_2S + 4\ H_2O \rightarrow 4\ NH_4Cl + 2\ H_2S\uparrow + \mathbf{H_4TiO_4}$$

$$TiCl_4 + 2\ BaCO_3 + 2\ H_2O \rightarrow 2\ BaCl_2 + 2\ CO_2\uparrow + \mathbf{H_4TiO_4}$$

4. **Chromotropic acid,** 1, 8-dihydroxynaphthalene-3, 6 disulfonic acid,



gives an intense brown coloration. It serves to detect 5 γ of TiO_2 in a drop. The color is weakened slightly by the addition of $SnCl_2$ which prevents interference by iron and uranium. To test for titanium and uranium in the presence of one another

use the aqueous extract from the melt obtained by fusing with $K_2S_2O_7$. Neutralize a little of the solution with NH_4OH, add a drop of Na_2S solution, mix with an excess of concentrated $(NH_4)_2CO_3$ solution, and filter. $Ti(OH)_4$ and various sulfides will be on the filter, and the uranium will pass into the filtrate. Moisten a filter paper with the filtrate and test for uranium on the filter with a drop of $K_4Fe(CN)_6$ solution. To test for titanium, take a little of the original sulfate solution, add some $SnCl_2$ solution, warm gently, and transfer a drop of the clear solution to a filter paper that has been touched with a 5 per cent solution of the sodium salt of chromotropic acid.*

5. **Cupferron** (cf. p. 214) precipitates the yellow titanium salt of phenylnitrosohydroxylamine from acid solutions:

$$Ti^{++++} + 4\ C_6H_5NO \cdot NO^- \rightarrow Ti(C_6H_5NO \cdot NO)_4$$

In the presence of tartaric acid, iron can be removed by ammonia and ammonium sulfide and the titanium precipitated in the acidified filtrate with cupferron.

6. **Ether** does not dissolve titanium chloride. By shaking a 6 *N* hydrochloric acid solution with ether, therefore, it is possible to separate ferric chloride from titanium chloride.

7. **Hydrogen Peroxide.** — If hydrogen peroxide is added to a slightly acid solution of titanium sulfate, the solution is colored orange-red, except in the presence of small amounts of titanium, when the color is light yellow. This reaction, which probably depends upon the formation of pertitanic acid or $H_2\left[Ti\begin{matrix}O\\ \diagup\ \diagdown\\ O\end{matrix}(SO_4)_2\right]$, is exceedingly delicate, and is especially suitable for the detection of titanium in rocks. As little as 2 γ of titanium in a drop of solution on a spot plate will give the test. Chromates, vanadates, molybdates, and ceric salts must be absent for they also give color with hydrogen peroxide.

If a solution of titanium sulfate is treated with a large excess of hydrogen peroxide and then potassium hydroxide is added, a precipitate is formed which dissolves in a great excess of the alkali, forming a yellow solution. This solution remains clear for a long time, but eventually a bright yellow precipitate is formed.

An insoluble titanium compound on being fused with sodium peroxide in a nickel crucible yields a melt which permits the extraction of all the titanium by water. If the solution is made strongly acid with sulfuric acid, the orange-red color of pertitanic acid is apparent. If iron was present in the original insoluble titanium mineral, it is left insoluble in water after the fusion with sodium peroxide.

Sodium peroxide added to a neutralized solution of titanium salt, followed by boiling, causes complete precipitation of the titanium as TiO_2. Pertitanic acid, like hydrogen peroxide, is not stable in hot, alkaline solutions.

In the Noyes and Bray scheme of analysis any titanium and zirconium that is not precipitated by hydrolysis during an early stage of the analysis (see 11) is thrown

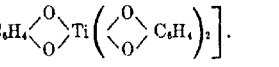
* N. A. Tananaev and G. A. Panchenko, *Z. anorg. allgem. Chem.*, **150**, 163–6 (1926).

down with the iron group by making a basic acetate separation at $p_H = 5.5$. The precipitate is dissolved in 6 *N* HCl, and gallium, together with iron, removed by shaking with ether. Then the solution is evaporated nearly to dryness with nitric acid, diluted with 10 ml of water, made alkaline with NaOH, and treated with Na_2O_2. By boiling and cooling, all the Ti, Zr, In, and rare earths are precipitated. This precipitate is treated with HCl and HF, which forms soluble H_2TiF_6, and insoluble fluorides of the rare earths. After filtering and evaporating with sulfuric acid, $Ti(SO_4)_2$ is obtained and the solution is tested for Ti and Zr as outlined under 11.

8. **Hyposulfurous Acid,** $H_2S_2O_4$, which can be obtained by the action of zinc on sulfurous acid, or its sodium salt, $Na_2S_2O_4$, gives a violet or reddish color with dilute solutions of titanium; the color is not taken up by shaking with ether. According to Brunck,* the following reaction takes place from left to right in acid solutions and from right to left in alkaline solutions.

$$2\ TiCl_4 + Na_2S_2O_4 \rightleftarrows 2\ TiCl_3 + 2\ NaCl + 2\ SO_2$$

9. **Potassium Ferrocyanide** produces in slightly acid solutions a brown precipitate.

10. **Pyrocatechol,** $C_6H_4(OH)_2$ or  , gives a yellow spot when a drop of a solution containing titanium is placed on filter paper which has been impregnated with freshly prepared 10 per cent aqueous solution of pyrocatechol. The test is obtained with 2.7 γ of titanium and is due to the formation of a complex compound having the formula  .

11. **Pyrosulfate-tannin.** — Titanium sulfate, obtained by fusion of titanium oxide with potassium pyrosulfate, dissolves in hot, 1 per cent tannin solution in 1.8 *N* sulfuric acid. In this respect titanium is like zirconium and differs from tantalum and columbium (niobium).

According to W. R. Schoeller,† this is the best way to separate titanium and zirconium from tantalum and columbium, a much cleaner separation being accomplished than by the salicylate treatment described in 13 on p. 551. The oxides of titanium and zirconium are sufficiently basic to form well-defined sulfates, whereas the earth acids, Ta_2O_5, and Cb_2O_5 are not. In the absence of tannin, the separation is not satisfactory because the basic oxides tend to form compounds with the earth acids so that some tantalum and columbium dissolves and some titanium and zirconium is precipitated. The tannin forms colored adsorption compounds with Ta_2O_5 and Cb_2O_5 (see p. 589).

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* *Ann. Chem.*, **346**, 283. Cf. R. Fresenius, *Z. anal. Chem.*, **24**, 410.

† *Analyst*, **54**, 453 (1929). Cf. Schoeller and Deering, *ibid*, **52**, 633 (1927).

To carry out the separation, fuse 0.1–0.2 g of the oxides with 2–3 g of potassium pyrosulfate in a silica crucible. Make the melt solidify in a thin layer along the sides of the crucible. When cold, treat with a hot, 1 per cent solution of tannin in 5 per cent sulfuric acid. Boil about five minutes. Filter, and treat the filtrate with H_2O_2 and Na_2HPO_4. (See 12.) For a confirmatory earth-acid test, see page 592.

12. **Sodium Phosphate** produces a precipitate in dilute sulfuric acid solutions:

$$Ti(SO_4)_2 + 2\,Na_2HPO_4 \rightarrow \mathbf{Ti(HPO_4)_2} + 2\,Na_2SO_4$$

Zirconium gives a similar reaction even in the presence of H_2O_2 which oxidizes the titanium to pertitanic acid and prevents its precipitation as phosphate. If zirconium is present, therefore, it can be separated from titanium by adding H_2O_2 and sodium phosphate. Then, if the precipitate of $Zr(HPO_4)_2$ is filtered off, the addition of Na_2SO_3 to the filtrate will cause the reduction of the titanium and its precipitation as phosphate. The combination of hydrogen peroxide and sodium phosphate in this way gives one of the best confirmatory tests for titanium. A suitable acid concentration is furnished by evaporating to fumes with 3 ml of 6 *N* H_2SO_4, cooling, and adding 5 ml of water, 10 ml of molar H_2O_2, and 10 ml of *N* Na_2HPO_4 solution.

13. **Sodium Thiosulfate** precipitates in boiling solutions all the titanium as metatitanic acid:

$$TiCl_4 + 2\,Na_2S_2O_3 + H_2O \rightarrow 4\,NaCl + 2\,S + 2\,SO_2\uparrow + \mathbf{H_2TiO_3}$$

14. **Water.** — Not only titanium acetate but also all titanium salts are hydrolytically decomposed by water.

The presence of tartaric acid, citric acid, and many other organic compounds prevents the above reactions. The neutralized, boiling tartrate or citrate solution containing ammonium acetate, when treated with tannin, gives an insoluble, voluminous, flocculent adsorption complex of a strikingly vivid red color.

The ease with which soluble titanium salts undergo hydrolysis with the formation of insoluble titanic acid is the basis of the oldest method for separating titanium from aluminum, iron, chromium, etc.; the oxides of these metals are fused with potassium pyrosulfate, the product of the fusion is dissolved in cold water,* and the solution is then heated to boiling. The titanium is completely precipitated as granular metatitanic acid, which can be readily filtered off, while the other metals remain in solution as sulfates:

$$Ti(SO_4)_2 + 3\,H_2O \rightleftarrows 2\,H_2SO_4 + H_2TiO_3$$

Since this reaction, like all hydrolytic decompositions, is reversible, it is evident that, in order to make the precipitation of the metatitanic acid complete, the *amount of free acid present should be kept small,*† *considerable water should be used, and the solution kept hot while filtering.*

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* Solution takes place much more quickly if the liquid is kept in constant motion, *e.g.*, by conducting a current of air through it.

† If too little acid is present, however, iron and aluminum will precipitate.

In the scheme of analysis devised by Noyes and Bray, a solid substance is treated with HBr and the arsenic, germanium, and selenium distilled off as bromides. Then the solution is evaporated with $HClO_4$ almost to dryness. This serves to precipitate oxides or phosphates of Sb, Sn, W, Ta, Cb, etc. Under ordinary circumstances, because hydrolyzed so readily, all but about 4 mg of Ti will be obtained in this residue. The presence of zirconium tends to prevent the complete precipitation of titanium, but both titanium and zirconium are precipitated here, for the most part, when phosphate is present. By treating the precipitate with hydrofluoric acid and evaporating with sulfuric acid, the above-mentioned oxides and phosphates are dissolved, and by treatment with NH_4OH and $(NH_4)_2S$, the Sb, Sn, W, (Mo) are converted into soluble thio-salts and a precipitate is obtained containing hydrated TiO_2, Ta_2O_5, Cb_2O_5, and possibly Zr. If this precipitate is boiled with a large volume of dilute sodium salicylate and salicylic acid solution (3 g Na_2CO_3 and 15 g salicylic acid in 400 ml of hot water) the TiO_2 dissolves as complex salicylate (Ti or TiO replacing the H of the phenol group in salicylic acid). Then, after filtering and evaporating the solution, the salicylic acid is removed by adding sulfuric acid and shaking with ether and the titanium is reprecipitated by evaporating and pouring into a slight excess of dilute NaOH. This precipitate is soluble in hot, 6 *N* HNO_3. The nitric acid solution will give the H_2O_2 test or the phosphate test for titanium.

15. **Zinc** or **Tin** produces in acid solutions, preferably hydrochloric acid, a violet color caused by the formation of $TiCl_3$:

$$2\,TiCl_4 + Zn \rightarrow ZnCl_2 + 2\,TiCl_3$$

The quadrivalent titanium compounds are *not* reduced by hydrogen sulfide or sulfurous acid.

Reactions in the Dry Way

Titanium compounds do not color the borax or sodium metaphosphate bead in the oxidizing flame; after continued heating in the reducing flame the bead becomes yellow while hot and violet when cold. By the addition of a little tin the violet color appears much more quickly. The addition of iron causes a brownish red bead.

On fusing titanic acid with sodium carbonate, sodium metatitanate is formed, which is soluble in hot, 6 *N* HCl. By treatment with *hot* water, sodium metatitanate is decomposed, forming metatitanic acid, which is difficultly soluble in dilute acids. Even in cold water, sodium titanate is hydrolyzed and does not dissolve.

ZIRCONIUM, Zr. At. Wt. 91.22, At. No. 40

Density 6.5. M. P. 1927°. B. P. 2900°

Occurrence. — Zircon, $ZrSiO_4$, tetragonal, isomorphous with rutile, Ti_2O_4; thorite (orangite), $ThSiO_4$; cassiterite, Sn_2O_4; polianite, Mn_2O_4, and plattnerite, Pb_2O_4. Baddeleyite, ZrO_2, monoclinic.

Zirconium was discovered by Klaproth in 1789 and owes its name to the Arabian word *zerk* = a precious stone. Two forms of the metal are known. The crystalline

form is white like cast iron, hard and brittle when about 99 per cent pure. Very pure zirconium, which is hard to obtain, is soft, ductile, and malleable. Amorphous zirconium is a black powder.

Properties. — Thin strips of zirconium burn in the air when lighted with a match. Heated in hydrogen zirconium forms a hydride and in nitrogen a nitride; both products are dissociated at 700°. Zirconium combines with halogens to form tetrahalides, but in many zirconium compounds the ZrO^{++} ion is present. Thus the salt $ZrOCl_2$ is properly called *zirconyl chloride* although it has been termed zirconium *basic chloride* and zirconium *oxychloride*.

Compact zirconium is hard to dissolve in acid, and alkali hydroxides react only slightly with the metal. Hydrofluoric acid and aqua regia dissolve the metal, and a mixture of nitric and hydrofluoric acid is very efficient although nitric acid alone has little effect. Hot concentrated sulfuric acid acts energetically upon it, forming water-soluble zirconium sulfate, $Zr(SO_4)_2$. There is little demand for metallic zirconium, but it is present in some steels.

Zirconium forms only one important oxide, the dioxide, ZrO_2. It can be dissolved by heating for a long time with a mixture of two parts of concentrated H_2SO_4 and one part of water and afterwards diluting. Zirconium forms four kinds of salts: normal salts, zirconyl salts, zirconates, and complex salts, *e.g.*, $ZrCl_4$, $ZrOCl_2$, Na_2ZrO_3, K_2ZrF_6. The amphoteric nature and the tendency to form complex salts are characteristic of quadrivalent zirconium.

The mineral zircon, $ZrSiO_4$, cannot be decomposed by heating with acids. It must be finely pulverized and fused with four times as much sodium carbonate at a high temperature in a platinum crucible; sodium silicate, Na_4SiO_4, and sodium zirconate, Na_2ZrO_3, are formed. On treating the melt with water, the former salt dissolves, while the latter is decomposed hydrolytically, forming sodium hydroxide and sandy, insoluble zirconium hydroxide; the latter retains some of the caustic soda very persistently. After washing the residue, heat it, without previous drying, with concentrated sulfuric acid at a temperature near the boiling point; in this way anhydrous $Zr(SO_4)_2$ is obtained. By pouring water over the latter, the salt $Zr(SO_4)_2 \cdot 4\,H_2O$ is formed, which dissolves slowly in cold water, but more readily in hot water, forming a solution with an acid reaction.

Zircon is also attacked by fusing with potassium acid fluoride; potassium fluorosilicate, K_2SiF_6, and potassium fluorozirconate, K_2ZrF_6, are formed. Heating with carbon, to form zirconium carbide, and then heating in a stream of chlorine, or heating with carbon tetrachloride at 450°, results in the sublimation of water-soluble zirconium chloride, $ZrCl_4$, which gives zirconyl chloride, $ZrOCl_2$, on treatment with a little water; this chloride is soluble in water but, unlike ferric chloride, is insoluble in ether.

Reactions in the Wet Way

A solution of zirconium nitrate, $Zr(NO_3)_4$, or a freshly prepared one of zirconyl chloride, $ZrOCl_2 \cdot 8\,H_2O$, may be used for the following reactions:

1. **Alkali Hydroxides** produce white, slimy $Zr(OH)_4$ precipitates insoluble in an excess of reagent (difference from Al and Be). When the zirconium hydroxide is produced in the cold it is readily soluble in dilute acids; but when thrown down from a boiling solution it is very difficultly soluble in dilute acids, though it will dissolve even then in concentrated acids without difficulty.

Tartaric acid prevents the above precipitation owing to the formation of the complex acid, $H_2[ZrO(C_4H_4O_6)_2]$, which gives soluble alkali salts. If ferric ions are present in the original solution, they can be precipitated by ammonium sulfide as ferric sulfide, and the zirconium, like aluminum and beryllium, remains dissolved. Tannin, in an alkaline tartrate solution, produces a dirty-white precipitate (difference from titanium).

2. **NH_4OH, $(NH_4)_2S$, or Na_2O_2** also produce white, slimy precipitates of $Zr(OH)_4$ insoluble in an excess of the reagent; the precipitate dissolves in a mixture of dilute hydrochloric and hydrofluoric acids (difference from rare earths which form insoluble fluorides by this treatment).

Boiling a dilute acetate solution (p_H = about 5.3) causes the precipitation of $Zr(OH)_4$. By the basic acetate precipitation, Fe^{+++}, Ga^{+++}, Cr^{+++}, Al^{+++}, In^{+++}, Ti^{++++}, and Zr^{++++} can be separated from Mn^{++}, Zn^{++}, Co^{++}, Ni^{++}, UO_2^{++}, Be^{++}, rare earths, and alkaline earths. If phosphate is present, however, some rare earth phosphates are likely to precipitate even when considerable ferric iron has been added to the solution.

3. **Alkali Carbonates** produce white precipitates somewhat soluble in an excess, but reprecipitated by ammonia.

4. **$(NH_4)_2CO_3$** produces a white, flocculent precipitate of basic carbonate, readily soluble in an excess of the reagent, but reprecipitated by boiling.

5. **Ammonium Oxalate** precipitates $Zr(C_2O_4)_2$ soluble in an excess of the reagent. From the solution in ammonium oxalate, zirconium is not precipitated on the addition of hydrochloric acid (difference from thorium).

Remark. — A solution of zirconium sulfate behaves quite differently from that of the nitrate and basic chloride towards oxalic acid and ammonium oxalate, a fact which, although published by Berzelius and also by Pfaff, had been entirely forgotten by most chemists until their attention was called to it by R. Ruer.*

On treating an aqueous solution of zirconium sulfate with oxalic acid or ammonium oxalate there is no precipitation; in fact, precipitation will not take place from nitrate or chloride solutions when these contain sufficient sulfuric acid, sodium, or ammonium sulfate.

The cause of this different behavior lies in the fact that zirconium forms complex compounds with sulfuric acid and alkali sulfates. Thus the solution of zirconium sulfate contains the acid $H_2[ZrO(SO_4)_2]$, and on treating a solution of zirconyl chloride or nitrate with sodium or ammonium sulfate (but not the potassium salt) the sodium or ammonium salt of this complex acid is formed:

$$ZrOCl_2 + 2\ Na_2SO_4 \rightarrow 2\ NaCl + Na_2[ZrO(SO_4)_2]$$

These compounds, however, are electrolytically dissociated in aqueous solution as follows:

$$H_2[ZrO(SO_4)_2] \rightleftarrows 2\ H^+ + [ZrO(SO_4)_2]^{--}$$

Since the zirconium is present in the anion it cannot react with oxalic acid.

* *Z. anorg. Chem.*, **42**, 85 (1904).

6. **$BaCO_3$** causes incomplete precipitation, even on boiling.

7. **Cupferron** precipitates zirconium completely from cold solutions containing 5–10 per cent by volume of concentrated sulfuric acid. The precipitate is white and curdy. (Separation from aluminum.)

8. **HCl.** — Ruer* recommends the following test for the identification of zirconium:

Precipitate the zirconium in the cold by ammonia, filter, wash, and separate it from the filter as completely as possible. Dissolve the precipitate in hydrochloric acid, or if small in amount treat the paper and precipitate together with not too strong HCl and filter. Evaporate the hydrochloric acid solution to dryness on the water bath and take up the residue in a little water. To the cold, saturated solution add hydrochloric acid drop by drop; the presence of zirconium will be indicated by the formation of a voluminous precipitate of zirconium oxychloride. Redissolve the precipitate by heating the solution, and allow the liquid to cool. After some time fine, silky needles of $ZrOCl_2 \cdot 8\ H_2O$ will precipitate.

Ignited zirconia, ZrO_2, is insoluble in hydrochloric acid. Fuse it with $KHSO_4$ in a silica crucible or transform it into zirconium sulfate by heating with concentrated sulfuric acid (2 : 1), dissolve this in water, precipitate the zirconium by ammonia, and carry out the above process.

9. **Hydrofluoric Acid** as a rule produces no precipitation (difference from thorium, cerium, and other rare earths). From concentrated zirconium solutions a voluminous precipitate may be obtained by the careful addition of hydrofluoric acid, but the precipitate is soluble in an excess of the reagent.

10. **H_2O_2** precipitates from slightly acid solutions white, voluminous zirconium peroxide, which evolves chlorine on being warmed with concentrated HCl. When both sodium phosphate and hydrogen peroxide are added to a solution containing Zr, the precipitate produced is $Zr(HPO_4)_2$. (H_2O_2 prevents precipitation of $Ti(HPO_4)_2$.)

11. **Oxalic Acid** gives a white, flocculent precipitate of zirconium oxalate, readily soluble in an excess of oxalic acid, difficultly soluble in dilute hydrochloric acid, and readily soluble in ammonium oxalate.

12. **Potassium Ferrocyanide** gives a white precipitate in neutral solutions and a greenish yellow precipitate of zirconium ferrocyanide in acid solutions. Sulfate solutions do not give the precipitation, or only to a slight extent.

13. **Potassium Sulfate.** — A cold, concentrated solution of K_2SO_4 precipitates, little by little, all the zirconium as potassium zirconium sulfate, insoluble in an excess of the reagent (difference from Al and Be). The precipitate, when produced in the cold, dissolves readily in considerable dilute HCl. If it is produced from a boiling solution, basic zirconium

* *Z. anorg. Chem.*, **42**, 85 (1904).

sulfate is formed by hydrolysis, which is quite insoluble in dilute HCl (difference from Th and Ce).

14. **Selenious Acid, H_2SeO_3,** is an excellent precipitant of zirconium as zirconyl selenite; on standing the precipitate becomes $Zr(SeO_3)_2$.

15. **Sodium Iodate** produces in slightly acid solutions a voluminous precipitate of zirconium iodate, soluble in hot, dilute HCl. The reaction is sensitive to changes in acidity, and since other insoluble iodates are known, it is of no practical value for detecting Zr although it has been recommended for separating zirconium from aluminum.

16. **Na_2SO_4** produces no precipitation, even on boiling a solution which is slightly acid with sulfuric acid (difference from Ti).

17. **$Na_2S_2O_3$** precipitates zirconium completely as the hydroxide; the precipitate is always contaminated by sulfur.

18. **Sodium Phosphate,** Na_2HPO_4, throws down white $Zr(HPO_4)_2$ even in solutions containing 20 per cent sulfuric acid by weight. No other element forms an insoluble phosphate under these conditions except titanium which can be kept in solution as pertitanic acid if sufficient hydrogen peroxide is added before the sodium phosphate.

19. **Turmeric Paper,** after being moistened with the hydrochloric acid solution of a zirconium salt and dried, is colored reddish brown (difference from Th).

Reactions in the Dry Way

ZrO_2 is infusible in the oxyhydrogen flame (difference from the other earths), but glows brightly.

THORIUM, Th. At Wt. 232.12, At. No. 90

Density 11.3–11.7. M. P. 1845°. B. P. > 3000°

Occurrence. — Thorite (orangite), $ThSiO_4$, with 50 to 58 per cent ThO_2; thorianite, a mineral discovered in Ceylon, with 72 to 76 per cent ThO_2 and 11 to 12 per cent UO_2.* Small quantities, up to about 8 per cent, of ThO_2 are found with gadolinite, $Y_2O_3 \cdot 3\,(Be, Fe)O \cdot 2\,SiO_2$; monazite, $(Ce,La,Nd,Pr)PO_4$; and in the rare columbates, samarskite, pyrochlore, euxenite, etc. Euxenite is essentially a titanate and columbate of Ce(La,Nd,Pr) and usually contains UO_2 and FeO. Thorite, monazite, and gadolinite are decomposed by acids, preferably sulfuric acid.

Preparation and Properties. — The impure metal itself has been obtained by heating $ThCl_4$ or K_2ThCl_6 with metallic sodium. In the air it is stable and exhibits radioactivity. Upon gentle heating it ignites and burns to the dioxide. The metal dissolves in hydrochloric acid with evolution of hydrogen; it is less readily dissolved by sulfuric acid and by hydrofluoric acid and is practically insoluble in alkali hydroxide solutions.

The element derives its name from *Thor*, a Scandinavian god. It was discovered by Berzelius in 1828. In the periodic classification (cf. p. 87), it is the heaviest

* *Chem.-Ztg. Rep.*, **1905**, 91.

member of Group IV. In this group the elements titanium, zirconium, hafnium, and thorium are closely related to one another. Like zirconium, the element is said to exist in two allotropic forms, one crystalline and the other amorphous. Like zirconium, the metal can be made to take fire in the air and burn to ThO_2. It also burns in chlorine, bromine, iodine, or sulfur vapors at 450°. Thorium is more electropositive than magnesium and alloys readily with other metals such as aluminum, copper, nickel, and zinc. Alloyed with tungsten it is used for making electric-light filaments.

The dioxide, ThO_2, is white when perfectly pure and is present in ignited gas mantles, being formed by the ignition of $Th(NO_3)_4$. A gas mantle made from pure thorium nitrate is only feebly luminous, with a slight reddish tint. Traces of CaO or CeO_2 cause it to glow much more brightly. The most brilliant light, which is slightly yellow, is obtained with about 1 per cent or more of CeO_2.

Ignited thorium dioxide, ThO_2, can be dissolved by fuming with concentrated sulfuric acid, cooling, and adding the acid to ice-cold water, or to dilute sulfuric acid; it is not soluble in other acids even after fusing with alkalies. Thorium shows a tendency to form colloidal solutions but less tendency to form complex ions than does cerium, zirconium, or titanium.

Commercial thorium nitrate with 48–49 per cent ThO_2 usually contains more than 5 per cent of $Th(SO_4)_2$. The presence of sulfate, however, cannot be detected unless the thorium is first removed by means of oxalic acid. The mixture of sulfate and nitrate melts when heated and decomposes, swelling up enormously and leaving behind a light, bulky white oxide that is soft to the touch. The oxide should remain perfectly white after several minutes' heating in the oxidizing flame of the Bunsen burner. If a pink tint is noticeable, a trace of didymium is present.

Reactions in the Wet Way

Use a solution of $Th(SO_4)_2$ or of $Th(NO_3)_4$.

Anhydrous thorium sulfate dissolves freely in ice water, but, on heating the concentrated solution, or even on standing at room temperature, the sparingly soluble hydrated salt $Th(SO_4)_2 \cdot 8\ H_2O$ or $Th(SO_4)_2 \cdot 9\ H_2O$ separates out (difference from Al, Be, Ti, Zr). This behavior can be used for separating thorium from small quantities of other rare earths. The hydrates with 8 or 9 molecules of H_2O are transformed above 45° into the bulky $Th(SO_4)_2 \cdot 4\ H_2O$, the solubility of which falls as the temperature rises. This is the stable phase in contact with the boiling solution.

1. **Alkali Carbonate** precipitates the white carbonate, soluble in an excess of the reagent, and not reprecipitated by the addition of ammonia. On boiling, the solution becomes turbid, but clears again on cooling.

2. **Ammonia, Ammonium Sulfide,** or **Alkali Hydroxide** produces a white precipitate of $Th(OH)_4$, insoluble in an excess of the reagent, but readily soluble in dilute acids when freshly precipitated. By boiling with thorium nitrate, or by treatment with a little aluminum chloride, ferric chloride, or hydrochloric acid, it is easy to obtain a colloidal solution of thorium hydroxide. Similarly by dialysis of thorium salts in pure water, it is easy to obtain a colloidal solution of the hydroxide. By igniting the hydroxide, ThO_2 is obtained, which is soluble in concentrated sulfuric acid only after long digestion.

3. $(NH_4)_2CO_3$ precipitates the white carbonate, readily soluble in an excess; on warming to 50° a basic carbonate is precipitated, which redissolves on cooling the solution. Ammonia causes no precipitation in this solution.

4. **Ammonium Oxalate** likewise precipitates thorium oxalate, which dissolves on boiling with a large excess of this reagent. The solution remains clear after cooling, provided the original solution did not contain too much free sulfuric acid, and enough ammonium oxalate was used. From the boiling solution of the ammonium double oxalate, HCl precipitates practically all the thorium as oxalate (difference from Zr).

In the presence of ammonium acetate, ammonium oxalate produces no precipitation; but by the addition of HCl almost all the thorium will be precipitated as oxalate.

5. $BaCO_3$ or $PbCO_3$ precipitates thorium ions completely in the cold, $Th(CO_3)_2$ being formed.

6. **HF** produces a white, gelatinous precipitate, which soon changes to a heavy powder. KF causes the same reaction.

7. **Hydrogen Peroxide** added to a hot, neutral solution, or to one which is faintly acid with H_2SO_4 or HNO_3, or even to an ammonium carbonate solution, precipitates all the thorium as white, hydrated thorium peroxide.

8. **Oxalic Acid** precipitates, from solutions which are not too acid, all the thorium as white, crystalline oxalate, practically insoluble in oxalic and dilute mineral acids.

The precipitate has the formula: $Th(C_2O_4)_2 \cdot 6\,H_2O$. It dissolves in ammonium acetate solutions containing a little free acetic acid. At the boiling temperature it dissolves in concentrated alkali oxalate solutions, particularly in ammonium oxalate, forming very stable complex ions: $[Th(C_2O_4)_4]^{--}$, $[Th(C_2O_4)_3]^{--}$, or $[Th_2(C_2O_4)_5]^{--}$. On cooling no precipitation takes place if sufficient ammonium oxalate was used. (Difference from the ions of Ce, La, Pr, Nd, and somewhat different from Y and Er.) The addition of hydrochloric acid causes the decomposition of the complex oxalate ion, and thorium oxalate is reprecipitated.

By gently igniting the oxalate, thorium dioxide is obtained and will give a colloidal solution with hydrochloric or nitric acid; the *sol* appears milky white by reflected light and a clear, yellow solution by transmitted light (looking through it).

9. **Potassium Azide,** KN_3, gives in faintly acid solutions a precipitate of hydroxide or of basic thorium azide with evolution of hydrazoic acid:

$$Th^{++++} + 4\,N_3^- + 4\,H_2O \rightarrow Th(OH)_4 + 4\,HN_3$$

According to Dennis* this is a characteristic reaction of thorium but

* *Z. anal. Chem.*, **34**, 82.

according to Curtius* zirconium also gives the test in the cold and yttrium on boiling.

10. **Potassium Ferrocyanide** gives a white precipitate in neutral or faintly acid solutions; in the former case the test is sensitive.

11. **Potassium Hydroxide** and **Chlorine** do not dissolve thoria.

12. **Potassium Iodate** gives a bulky, white precipitate of $Th(IO_3)_4$ even when 50 per cent by volume of concentrated nitric acid is present; chloride must be absent. Zirconium and quadrivalent cerium are precipitated similarly, but the iodates of the trivalent rare earths are readily dissolved by nitric acid. This is a sensitive test for thorium; the precipitate may be freed from traces of other iodate (except of Zr or Ce) by treating with a few milliliters of a hot solution of 4 g KIO_3 in 500 ml of 1.2 *N* HNO_3.

13. **Potassium Sulfate** precipitates $K_4Th(SO_4)_4 \cdot 2H_2O$, difficultly soluble in water and insoluble in concentrated K_2SO_4 solution (difference from Y). The corresponding sodium compound is fairly soluble in water.

14. **Sodium Hypophosphate,** $NaHPO_3$, produces a white, flocculent precipitate of thorium hypophosphate by boiling in the presence of considerable hydrochloric acid.

15. **Sodium Thiosulfate** precipitates all the thorium on boiling.

There are no characteristic dry reactions.

HAFNIUM, Hf. At. Wt. 178.6, At. No. 72

This element belongs to the fourth group in the periodic system, lying between zirconium, which it resembles most closely, and thorium. It has been found, with the aid of Röntgen ray spectra, in nearly all zirconium minerals. It can be separated from zirconium only by means of repeated fractional precipitations. Thus K_2HfF_6 is somewhat more soluble in water than K_2ZrF_6, and $HfOCl_2$ is less soluble than $ZrOCl_2$. The hydroxide, $Hf(OH)_4$, is more basic than $Zr(OH)_4$ and, therefore, is less readily precipitated by NH_4OH or $Na_2S_2O_3$. Moreover, $Hf(SO_4)_2$ is stable up to 500° whereas $Zr(SO_4)_2$ decomposes at 400°. The density of ZrO_2 is 5.73 and of HfO_2 is 9.67 so that the Hf content of mixtures can be estimated by the density.

* *Ibid.*, **38**, 49.

RARE EARTH METALS

By *rare earths* is understood a group of oxides which are obtained in hydrated form as gelatinous precipitates upon adding ammonium hydroxide or caustic alkali to a solution of their salts. In the periodic table, the rare earth metals are numbered 21 scandium, Sc; 39 yttrium, Y; 57 lanthanum, La; 58 cerium, Ce; 59 praseodymium, Pr; 60 neodymium, Nd; 61 illinium, Il; 62 samarium, Sm; 63 europium, Eu; 64 gadolinium, Gd; 65 terbium, Tb; 66 dysprosium, Dy; 67 holmium, Ho; 68 erbium, Er; 69 thulium, Tm; 70 ytterbium, Yb; and 71 lutecium, Lu.

These elements do not fit very well into the families or groups of the periodic classification. Moreover, their chemical and physical characteristics are so similar that it is, as a rule, impossible to separate one of these rare earths from its neighbors in the above arrangement by a single precipitation.

Previous editions of this book have classified these elements into two groups: (*a*) the gadolinite or yttrium earth metals — scandium, yttrium, europium, gadolinium, terbium, holmium, erbium, thulium, ytterbium, and lutecium, and (*b*) the cerite metals — cerium, lanthanum, praseodymium, neodymium, and samarium.

The gadolinite metals, or yttrium earths, constitute a group of trivalent elements that occur as silicates in the minerals gadolinite and rowlandite, as phosphates in xenotime, and as niobates in euxenite, yttrotantalite, and certain other rare minerals. In these minerals the elements scandium, yttrium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium preponderate over certain other rare elements which occur with them and which are markedly different in their chemical behavior, namely, the *cerite metals*. Of all the elements in the group, yttrium and then erbium occur in the largest quantities and may be regarded as the two most important elements. Scandium, however, is also quite widely distributed and has been found recently in certain tungsten and tin ores. The remaining elements are extremely rare in occurrence. In occurrence and chemical properties europium, gadolinium, and terbium are very similar; so are dysprosium, holmium, erbium, and thulium as well as ytterbium and lutecium.

The cerite metals occur to some extent in the minerals just mentioned. Cerium itself is the most abundant and most important element of the entire rare earth group. The cerite metals occur in larger quantities as silicates in the minerals cerite, $H_3Ca(CeAl)_3Si_3O_{13}$, and orthite (allanite), $HCa_2Ce_3Si_3O_{13}$, as phosphates in monazite, as columbates and tantalates in æschynite, as fluoride in fluorcerite, and in a number of rarer minerals of similar composition.

The best way of attacking the minerals is by treatment with concentrated sulfuric acid. The silicates cerite, orthite, and gadolinite can be decomposed by repeated evaporation with strong hydrochloric acid. The phosphates (monazite, xenotime, etc.), are not decomposed well by hydrochloric acid; after heating with concentrated sulfuric acid, some of the excess sulfuric acid should be volatilized and the moist mass stirred slowly into cold water. The columbates, tantalates, and titanates (fergusonite, euxenite, æschynite, etc.), are best fused with five or six times as much sodium acid sulfate; after cooling the melt, a few drops of concentrated acid are added to replace that lost by volatilization and the solid is then treated with water

which causes the separation of columbic and tantalic acids. Hydrofluoric acid also is useful in attacking most of these minerals, the action taking place even when cold; the earth acids go into solution, and the earth fluorides are left undissolved.

It is characteristic of the rare earths that they are precipitated by oxalic acid and by hydrofluoric acid from distinctly acidic solutions and the entire group can be separated from other substances by repeating this precipitation. Scandium fluoride, however, is somewhat soluble in an excess of hydrofluoric acid. The carbonates and phosphates are also insoluble in water.

The metals themselves are obtained by electrolysis of the fused chlorides or fluorides. They are white or pale yellow and fairly stable in the air. The density lies between 6.15 (lanthanum) and 7.7 (samarium), that of cerium being 7.04. They are good reducing agents and have been used as such in place of metallic magnesium. Yttrium itself has not been obtained perfectly pure. In the impure state it is a gray powder capable of being polished. It has a high melting point and burns to the oxide. It can be prepared by electrolysis of fused sodium yttrium chloride or by reduction with metallic magnesium.

Metallic cerium is strongly pyrophoric; it gives sparks when struck or rubbed against steel. A pyrophoric alloy of cerium and iron is used in gas lighters. The metals all burn in oxygen and give a bright light. They decompose water slowly and dissolve readily in acid with liberation of hydrogen.

The trivalent elements scandium, yttrium, lanthanum, gadolinium, ytterbium, and lutecium are undoubtedly homologues of aluminum. Their oxides and salts are white. Sc_2O_3 has weakly basic properties, but La_2O_3 is about as strongly basic as CaO.

Of the elements of the gadolinite group, yttrium is always the last to precipitate as hydroxide and the last to decompose upon the ignition of the nitrates. The only gadolinite earth known to give an oxide higher than that of the trivalent metal appears to be terbium, which has the oxide Tb_4O_7, a black substance when pure but causing other oxides of the group to appear yellow when it is present in small quantities. Heated in the non-luminous flame, yttrium oxide glows with a white light and erbium oxide gives a strong green light.

Excepting scandium, the salts of these metals are not readily hydrolyzed even when the acid is weak. The tendency to form complex salts is less than that of thorium and zirconium but greater than that of the cerite earths. Particularly important for separating yttrium earths from cerite earths is the greater solubility of the double sulfates. It is difficult to obtain double nitrates at ordinary temperatures. The chlorides crystallize with six molecules of water and when heated to 120° lose water and hydrochloric acid and are converted into insoluble basic chlorides of the YOCl type. The chlorides are more soluble in pyridine than the chlorides of the cerite metals. The anhydrous chlorides are not easily volatilized, but yttrium and scandium form the most volatile chlorides of the group.

In the cerite series a mixture of the oxides, as obtained by ignition of the oxalates from one of the typical minerals, has a brownish red color and may be regarded as containing salts of the trivalent metals with quadrivalent cerium as acidic constituent, the latter being the only member of the group which is known to form a stable oxide or salt that contains other than trivalent metal. At higher temperatures the oxides become crystalline, and at the temperature of the electric arc they are slightly volatile. The oxides dissolve in acid more readily than the oxides of the yttrium series, and although the solubility is affected by the previous treatment, the ignited oxides dissolve in acid unless more than 50–55 per cent of ceric oxide, CeO_2, is present.

The cerite earths form strong bases and set free ammonia from ammonium salts even when cold. Lanthanum hydroxide is about as basic as calcium hydroxide, but the basicity decreases in the following order — trivalent cerium, praseodymium, neodymium, samarium. Quadrivalent cerium forms an amphoteric hydroxide, and its basicity lies between that of the hydroxides of zirconium and thorium.

The chlorides of these trivalent elements usually crystallize with six molecules of water; praseodymium chloride, however, has seven molecules of water of crystallization. The nitrates also crystallize with six molecules of water. They form double salts of the type $R(NO_3)_3 \cdot 2\,NH_4NO_3 \cdot 6\,H_2O$; the stability and insolubility of the salt decrease with rise in atomic weight from lanthanum to samarium. Upon heating the chlorides or nitrates, insoluble basic salts, ROX, are formed (difference from yttrium earths); the salts of the metals with low atomic weight are the most stable.

The sulfates crystallize with four, eight, nine, or twelve molecules of water. Heating them to 400° or 500° causes the formation of anhydrous sulfates which dissolve freely in ice water. The concentrated solutions thus formed are, at room temperature, supersaturated with respect to certain of the hydrated salts which separate out on standing or on agitating the solutions. The solubility of these hydrated sulfates usually diminishes with rise of temperature. This property is sometimes utilized for separating rare earths from other elements.

The carbonates of the cerite metals dissolve more or less readily in concentrated solutions of $(NH_4)_2CO_3$, Na_2CO_3, and K_2CO_3, forming difficultly soluble double salts of which the potassium compounds are much more soluble than those with sodium or ammonium. Cautious dilution of the potassium carbonate solution causes precipitation of the crystalline double carbonates in the order La, Pr, Ce, Nd; the lanthanum double carbonate is first to precipitate, but it is prone to form supersaturated solutions.

Of the cerite series, the most basic element, lanthanum, gives the most soluble oxalate.

SCANDIUM, Sc. At. Wt. 45.10, At. No. 21

This element is found associated with other rare earths as well as in ores of tin, tungsten, and zirconium. Its properties were predicted ("eka-boron") by Mendelejeff prior to its discovery by Nilson in 1879. It belongs in the boron-aluminum family of the periodic system, but its salts also resemble those of bivalent beryllium and quadrivalent thorium and zirconium. Its salts are easily hydrolyzed.

For the purification of scandium salts the difficultly soluble $Sc_2(SO_4)_3 \cdot 3\,K_2SO_4$, $Sc_2(CO_3)_3 \cdot 4\,Na_2CO_3 \cdot 6\,H_2O$, or ScF_3 is prepared; the last-mentioned salt is quite soluble in concentrated alkali fluoride solutions, forming double fluorides such as NH_4ScF_4, so that it is easy to remove scandium fluorides from the fluorides of the other rare earths. The oxalate, $Sc_2(C_2O_4)_3 \cdot 5\,H_2O$, is much more soluble in dilute mineral acids than the other rare earth oxalates and is precipitated fairly completely only by the addition of a large excess of oxalic acid to an acid solution; an excess of alkali oxalate dissolves the scandium oxalate precipitate.

Like zirconium and thorium, scandium hydroxide is precipitated by boiling with sodium thiosulfate solution which also differentiates this element from the other rare earths.

Scandium, like titanium, can be separated completely from zirconium by adding hydrogen peroxide and sodium phosphate to an acid solution: $ZrHPO_4$ is precipitated while Sc and Ti remain dissolved. When the solution is subsequently treated with

sulfite to destroy the hydrogen peroxide, scandium is likely to precipitate with the $TiHPO_4$ although its phosphate is much more soluble.

Scandium, like zirconium, can be separated from titanium by dropping the acid solution into cold 3 per cent hydrogen peroxide containing ammonium hydroxide; titanium remains in solution as pertitanic acid.

Scandium is not precipitated with thorium or quadrivalent cerium by potassium iodate in the presence of fairly strong nitric acid, unless more than 30 mg of Sc are present.

When a solution of NH_4ScF_4 is fumed with concentrated sulfuric acid, $Sc_2(SO_4)_3$ separates out. This behavior distinguishes scandium from titanium and zirconium but not from other rare earths. By diluting with cold water the $Sc_2(SO_4)_3$ passes into solution, and by the addition of NH_4OH, insoluble $Sc(OH)_3$ is formed. If this is dissolved in HCl and the $ScCl_3$ solution is evaporated, 1 drop of 27 *N* HF will give a precipitate of ScF_3 which can be distinguished from other rare earth fluorides by its solubility in acid ammonium fluoride solution.

YTTRIUM, Y. At. Wt. 88.92, At. No. 39

Density 4.57

Occurrence. — Yttrium is an important constituent of gadolinite, $Y_2O_3 \cdot 3\,(Be,Fe)O \cdot 2\,SiO_2$, and of yttrotantalite, $Y_4[(Cb,Ta)_2O_7]_3$, an isomorphous mixture of yttrium pyrotantalate and pyrocolumbate. The elements of this group are also found in cerite, thorite, and monazite.

Yttrium oxide, Y_2O_3, is white when pure but yellow when contaminated by other oxides of the group.

The hydroxides of the yttrium earths are bases whose strengths lie between that of the alkaline earth and aluminum groups; yttrium is the most basic, and probably the others can be grouped in the following order: gadolinium, terbium, erbium, ytterbium, . . . scandium. Owing to the somewhat different position in the periodic table, it is probable that the elements between yttrium and scandium are more closely related to one another and for the same reason scandium in some respects is similar to beryllium and in other respects to thorium and zirconium. In the fractional precipitation by bases or in the decomposition of the nitrates by ignition, the elements show the same gradation of properties — yttrium is always the last to precipitate and the last to decompose. Its separation from the other yttrium earths is usually based upon the fact that the last fractions are invariably rich in yttrium.

Yttrium oxide, Y_2O_3, is the principal constituent of the so-called *yttrium earths*. It is more basic than the other yttrium earths and in the fractional precipitation by bases, or in the decomposition of the nitrates by ignition, yttrium is the last to precipitate and the last to decompose. The following reactions, however, are common to all the yttrium earths except as noted. It is assumed that a solution of $Y(NO_3)_3$ is used.

Reactions in the Wet Way

1. **HF** produces white amorphous YF_3, which becomes pulverulent on warming and is insoluble in water and in HF (difference from Al, Be, Ur, and Ti).

The precipitate is soluble in mineral acids if it has not been ignited; after strong heating it is less soluble.

Scandium fluoride is not dissolved much by concentrated hydrochloric acid, and after being ignited it requires concentrated sulfuric acid to attack it. Scandium fluoride, like zirconium fluoride, forms easily soluble double fluorides and thus differs from the other rare earth fluorides.

2. HIO_3 or KIO_3 gives a precipitate that is readily soluble in nitric acid even in the presence of an excess of the precipitant (difference from thorium and zirconium).

3. H_2O_2 in alkaline solution causes the formation of gelatinous, very unstable hydrated peroxide $Y(O \cdot OH)(OH)_2$.

4. K_2CO_3 and Na_2CO_3 precipitate the white carbonate, readily soluble in excess; after standing some time an insoluble double salt separates out.

The solubility of the carbonate in excess of the precipitant is much greater than that of the cerite earths, and this serves as a basis of separation. Yttrium carbonate dissolves more readily in potassium bicarbonate and in ammonium carbonate than in normal potassium carbonate, but the solubility is not as great as that of the corresponding beryllium precipitate.

Erbium behaves like yttrium, only the solution does not become turbid on standing.

5. **KOH** and **NaOH** precipitate the white hydroxide, insoluble in an excess; the presence of tartaric acid does not prevent precipitation, but in this case yttrium tartrate is precipitated (difference from Al, Be, Th, and Zr). On igniting the precipitate, the oxide is obtained, which is readily soluble in acids.

The hydroxides precipitated from hot solutions are gelatinous but easy to filter; from cold solutions they are slimy and hard to wash. The hydroxides of yttrium and of erbium absorb carbon dioxide from the air.

6. K_2SO_4 forms a double salt which is soluble in K_2SO_4 solution (difference from Zr, Th, Ce, La, Nd, and Pr).

Within the group of yttrium earths (disregarding the very slightly soluble scandium double sulfate) the double sulfates of europium, gadolinium, and terbium are the least soluble; they occupy a position intermediate between the cerite earths and the other yttrium earths.

7. $(NH_4)_2CO_3$ produces a white precipitate of the carbonate, readily soluble in an excess of the reagent; after standing some time the solution becomes turbid, owing to the deposition of a double salt, $Y_2(CO_3)_3 \cdot 2\ (NH_4)_2CO_3 \cdot 2\ H_2O$.

With erbium the solution does not become turbid on standing.

The solution of the pure hydroxide dissolved in excess of ammonium carbonate gives complete precipitation upon boiling, but if ammonium chloride is present it serves to decompose the precipitate upon further boiling, with liberation of ammonia, and the yttrium goes back into solution.

8. NH_4OH and $(NH_4)_2S$ precipitate the white hydroxide, insoluble in an excess.

In the presence of tartaric or citric acid no hydroxide is precipitated but the addition of ammonium hydroxide to a tartaric acid solution causes the formation of a white flocculent precipitate of ammonium double tartrate.

9. $NaHPO_3 \cdot 2\ H_2O$ does not give a precipitate in strong hydrochloric acid solutions (difference from thorium).

The absorption spectra are especially important in the examination of this group

of metals, furnishing, in fact, about the only means of controlling the purification by fractionation. The most important bands for erbium lie at 653, **523, 487, 450,** and 442 mμ; for dysprosium at 753, 475, 451.5, 427.5 mμ. Yttrium solutions do not give an absorption spectrum.

The color of the oxides and salts often helps to identify these elements. Thus erbium oxide is pink, and so are the solutions of its salts. Europium salts are slightly pink, but salts of holmium are distinctly so. Salts of dysprosium and thulium are light green or bluish green. The oxides and salts of the remaining metals are white or colorless.

10. **$Na_2S_2O_3$** does not cause precipitation in a boiling solution.

Scandium is the only member of the yttrium group to behave like aluminum, thorium, titanium, and zirconium.

11. **Oxalic Acid** precipitates white yttrium oxalate, insoluble in an excess, difficultly soluble in HCl, and perceptibly soluble in ammonium oxalate.

In erbium solutions, oxalic acid produces a light red, pulverulent precipitate; otherwise the reaction is the same as with yttrium. This is an important characteristic of the entire group of rare earths (except zirconium) which serves to distinguish them from aluminum and beryllium. The solubility of the yttrium earth oxalates is, in general, greater than that of the cerite earths, and, by boiling with concentrated alkali oxalate, the yttrium earth oxalates, particularly scandium oxalate, dissolve more readily than the oxalates of the cerite group; upon diluting and cooling there is usually complete reprecipitation (difference from thorium).

Reactions in the Dry Way

Yttrium oxide is strongly luminous on being heated; otherwise there is no reaction.

Erbium oxide, on being heated on a platinum wire, colors the flame distinctly green. If the light is viewed through a spectroscope, a number of bright lines will be seen in the dark green which approximate closely in position to the dark lines obtained in the absorption spectrum.

EUROPIUM, Eu. At. Wt. 152.0, At. No. 63

This element occurs to the extent of about 0.002 per cent in monazite sand. In its properties it lies between samarium (of the cerite group) and gadolinium, although this would not be indicated by the atomic weights. A pure salt has been obtained by recrystallizing the magnesium-bismuth-europium triple nitrate. The oxide, Eu_2O_3, and the salts are pink. The absorption spectrum is relatively weak showing lines at $\lambda = 579$, 526, 400–393, 376–374, 364–361 mμ. Europium and samarium both form bivalent chlorides by heating the trivalent chloride in dry hydrogen.

GADOLINIUM, Gd. At. Wt. 156.9, At. No. 64

Salts of this element are hard to differentiate from those of europium and terbium; even the separation by partial decomposition of the ignited nitrates or by means of magnesium bismuth complex nitrates is difficult.

The oxide and its salts are colorless; in the spectrum there are four strong absorption bands in the ultraviolet at $\lambda = 311$, 306, 305.5, and 305 mμ. Gadolinium oxide is almost as strongly basic as Y_2O_3.

TERBIUM, Tb. At. Wt. 159.2, At. No. 65

This element was isolated from the other rare earths by Urbain, by crystallizing repeatedly the bismuth double nitrate and the ethylsulfate compound. The oxide, Tb_2O_3, is white and the solutions are colorless although when concentrated they show a weak absorption band at $\lambda = 488$ mμ. The higher oxide, TbO_2, is black when pure but is yellow or cinnamon brown when impure. Brauner has suggested that this element is allied to cerium and thorium.

DYSPROSIUM, Dy. At. Wt. 162.46, At. No. 66

This element has been separated by crystallization of the ethylsulfate compound and of the bismuth nitrate double salt. The colorless oxide, Dy_2O_3 forms greenish yellow salts which show diffuse absorption bands at $\lambda = 753$, 475, 451, and 427 mμ.

HOLMIUM, Ho. At. Wt. 163.5, At. No. 67

A pure salt of this element has been prepared by crystallizing the *m*-nitrobenzenesulfonate. The oxide Ho_2O_3 is pale yellow and the salts are light orange in color. The principal absorption bands lie at $\lambda = 639$–640, 536, 486–485, 453–449, 420–417 mμ.

ERBIUM, Er. At. Wt. 167.64, At. No. 68

This element was separated in 1908 by Hofmann from the weakly basic portions of the yttrium earths by combining the operations of (*a*) decomposition of the nitrates by ignition, (*b*) formate crystallization, (*c*) ethylsulfate crystallization, etc. The oxide Er_2O_3 has a beautiful, delicate pink color, and so have the salts. There is a very beautiful absorption spectrum at $\lambda = 653$–651, 541, 523, 491–487, 453–450; at 420 mμ a weaker band is visible.

THULIUM, Tm. At. Wt. 169.4, At. No. 69

This element lies between erbium and ytterbium with respect to its basic nature; it has been prepared by fractional precipitation of the bromate. The salts are bluish green in color and show absorption stripes at $\lambda = 702$, 684, and 464 mμ.

YTTERBIUM, Yb. At. Wt. 173.04, At. No. 70

In the weakest basic part of the yttrium earths, this and the following element are found. They have been isolated as pure salts by fractionation of the ammonium double oxalate and by repeated crystallization of the nitrate in nitric acid solution. The element has also been called *aldebaranium*.

LUTECIUM, Lu. At. Wt. 175.0, At. No. 71

Salts of this element are obtained as explained under *ytterbium*. It has been called *cassiopeium*.

CERIUM, Ce. At. Wt. 140.13, At. No. 58

Density 6.9. M. P. 640°

Cerium forms two oxides, Ce_2O_3 and CeO_2; the former is basic and the latter is amphoteric. The cerous salts are white; the ceric, orange-red. The cerous solutions are colorless and have a sweet but astringent taste.

A. Cerous Salts

Reactions in the Wet Way

A solution of cerous nitrate, $Ce(NO_3)_3$, should be used.

1. **Bromine** behaves like chlorine except that an excess of this oxidizing agent does not dissolve the precipitate. (Difference from lanthanum and didymium.)

2. **Chlorine.** — If a cerous salt is treated with an excess of alkali hydroxide and then with chlorine gas, a yellow precipitate of $CeO_2 \cdot 3\,H_2O$ is obtained. If the chlorine gas is passed through the solution for a long time, the precipitate will redissolve.

3. **HF** produces in neutral and slightly acid solutions of cerous salts a gelatinous precipitate which by long digestion with the hot solution gradually becomes pulverulent. The precipitate of $CeF_3 \cdot H_2O$ is practically insoluble in water and dilute hydrofluoric acid, but fairly soluble in other mineral acids (difference from Al, Be, Zr, and Ti).

4. **H_2O_2.** — If a cerous salt is precipitated with ammonia and an excess of H_2O_2 is added, a reddish brown precipitate of *perceric hydroxide*, $CeO_3 \cdot nH_2O$ or $[Ce(OH)_3 \cdot O \cdot OH(?)]$, is formed, which is not very stable. On boiling the mixture for a while, the excess of H_2O_2 and the precipitate both decompose, leaving pure yellow $Ce(OH)_4$.

This can be made a very delicate test for traces of cerium in rare earth solutions as follows: Add the H_2O_2 and very dilute ammonia, drop by drop, to the neutral or faintly acid solution until a slight permanent precipitate is formed. If Ce is present, the feebly basic perceric hydroxide is thrown out first as a reddish brown precipitate; in the absence of Ce the precipitate is bluish white.* A sensitive alternative procedure is to replace the ammonia by excess of an alkali acetate and warm the solution to 50° or 60°, when any cerium separates out as reddish brown *basic perceric acetate* (Hartley's reaction).†

H_2O_2 can be used in color tests for traces of cerium. If an excess of warm, very concentrated *potassium* carbonate is added to a rare earth solution until the initial precipitate redissolves, the solution will turn yellow on the addition of H_2O_2 if even a trace of cerium is present. By cautious dilution with water until most of the other carbonates are precipitated, the yellow tint of the supernatant liquid can be readily observed.‡ When large amounts of cerium are present the gradual addition of H_2O_2 turns the solution through orange-red to a deep blood-red color, owing to the formation of *potassium perceric carbonate;* more H_2O_2 then lightens the color and throws down the Ce as a yellow precipitate, apparently a derivative of CeO_4.

The preceding potassium carbonate solution can be oxidized merely by passing air through it, but then the final product is *ceric potassium carbonate* and the solu-

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* Marc, *Ber.*, **35**, 2370 (1902).

† Hartley, *J. Chem. Soc.* **41**, 202 (1882).

‡ Job, *Compt. rend.*, **126**, 246 (1898); R. J. Meyer, *Z. anorg. Chem.*, **41**, 94 (1904).

tion turns yellow whatever the proportion of cerium may be. The first action of the air is to oxidize part of the cerium to the perceric stage; but the perceric salt immediately reacts with unchanged cerous salt to form ceric salt, which is stable toward oxygen.

Instead of using potassium carbonate, an excess of tartaric acid may be added to a rare earth solution, followed by ammonia. When this solution is boiled in contact with air, it turns yellow to brown in color if traces of cerium are present; the oxidation of the cerium is more rapidly effected by the addition of a little H_2O_2.*

5. **K_2CO_3** or **$(NH_4)_2CO_3$** produces a white precipitate insoluble in an excess of the reagent. The precipitate is amorphous at first but gradually becomes crystalline. In concentrated solutions of alkali carbonates, very slightly soluble double salts are formed, the potassium salt being the most soluble.

6. **K_2SO_4.** — If a *neutral* solution of cerous salt is treated with solid K_2SO_4 until no more is dissolved, $Ce_2(SO_4)_3 \cdot 3\ K_2SO_4$, a crystalline precipitate is slowly formed at room temperature, or more quickly on heating. All the cerium can be precipitated in this way, since the double sulfate is insoluble in concentrated potassium sulfate solution, but it is slightly soluble in pure water and more readily in acids. From slightly *acid* solutions, cerium can be completely precipitated with K_2SO_4 as $Ce_2(SO_4)_3 \cdot 2\ K_2SO_4 \cdot 2\ H_2O$. (Difference from Al, Be, and yttrium earths.)

Na_2SO_4 behaves similarly (difference from Th and Zr).

7. **NaOH** or **KOH** also precipitates white $Ce(OH)_3$, even in the presence of tartaric acid, etc. The white $Ce(OH)_3$ becomes yellow gradually on standing in the air, on account of being oxidized to $Ce(OH)_4$.

8. **$Na_2S_2O_3$** gives no precipitate even in boiling solutions of cerous salts.

9. **NH_4OH** and **$(NH_4)_2S$** each produces a white precipitate of $Ce(OH)_3$, insoluble in an excess of the reagent, but readily soluble in acids. The white $Ce(OH)_3$ becomes a bluish gray, bluish violet, and finally yellow on standing in the air, as it slowly oxidizes to $Ce(OH)_4$. In the presence of tartaric and citric acids, etc., the above reagents cause no precipitation (difference from Y).

10. **Oxalic Acid** or **Ammonium Oxalate** precipitates white cerous oxalate, insoluble in an excess of the reagent, and in dilute mineral acids. On ignition, pale yellow, insoluble CeO_2 is formed.†

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* Wirth, *Chem. Zeit.*, **37**, 773 (1913).

† Only when the cerous oxalate is pure. If it contains traces of praseodymium, the CeO_2 will have a deep yellow, terra-cotta, or salmon-pink tint; with larger amounts of praseodymium, the color becomes cinnamon-brown.

11. **Oxidation.** — Cerous salts can be oxidized to ceric salts in acid solutions (*a*) by heating with PbO_2 and HNO_3 (1 : 2); (*b*) by heating with ammonium persulfate; (*c*) by electrolysis; (*d*) by $NaBiO_3$. In all cases, the solution becomes yellow or orange in color.

B. Ceric Salts

A solution of orange-red ceric nitrate, $Ce(NO_3)_4$, or ceric ammonium nitrate, $Ce(NH_4)_2(NO_3)_6 \cdot H_2O$, can be used for the following reactions. Ceric sulfate is yellow and yields a deep yellow solution; the phosphate and iodate are also yellow. Recently ceric sulfate has been advocated as an oxidizing agent to be used in place of $KMnO_4$ or $K_2Cr_2O_7$. In the quadrivalent state, cerium is very easily reduced, even by hot hydrochloric acid solutions.

Preparation of Ceric Compounds. — As has been already stated, cerous hydroxide on standing in the air gradually turns yellow, on account of the formation of ceric hydroxide. This oxidation takes place immediately on the addition of chlorine or hypochlorite. If the solution of a cerous salt is treated with caustic potash solution and chlorine is conducted into it, the white cerous hydroxide which was at first formed is quickly changed to light yellow ceric hydroxide. This dissolves in dilute acids, forming orange solutions. It dissolves in concentrated hydrochloric acid with evolution of chlorine, forming *cerous* chloride. If white cerous hydroxide is heated in the air, it loses water and is changed into CeO_2, which is nearly white when cold, dark orange when hot, and is almost entirely insoluble in concentrated hydrochloric and nitric acids. In the presence of reducing substances (such as KI, $FeSO_4$, etc.) it dissolves in acids, forming cerous salts:

$$2\,CeO_2 + 8\,HCl + 2\,KI \rightarrow 2\,KCl + 4\,H_2O + I_2 + 2\,CeCl_3$$

If CeO_2 is heated gently with a slight excess of concentrated sulfuric acid, it is converted quantitatively to ceric sulfate, $Ce(SO_4)_2$. This is, perhaps, the most convenient way to prepare a solution of ceric salt. If the heating takes place with considerable sulfuric acid at its boiling point, decomposition results and cerous sulfate is formed with liberation of oxygen. A ceric solution can also be prepared by oxidizing the nitric acid solution with sodium bismuthate in the cold.

If a mixture of cerous and praseodymium hydroxides is ignited in the air, a cinnamon-colored mass is obtained, which contains all the cerium as dioxide and is readily soluble in dilute acids, forming ceric salts. If concentrated HCl is used, there is an evolution of chlorine, the ceric salt being reduced to cerous chloride. Concentrated nitric acid dissolves it, forming cerous and ceric salts; a distinct evolution of oxygen can always be detected.

The reason why the brown mass containing a little praseodymium dissolves although the pure oxide does not, is probably that CeO_2, like MnO_2 and PbO_2 (see pp. 219 and 111), plays the part of an acid anhydride, so that the brown mass contains the praseodymium as the salt of ceric acid. On treating this salt with a stronger acid, the praseodymium salt of the latter is formed, setting free ceric acid (ceric hydroxide), which in the hydrated form is readily soluble in acids, forming ceric salts.

Basic Ceric Salts. — If a solution of ceric nitrate is evaporated on the water bath to a consistency of sirup, the mass dissolves readily in water after it has become cold, and the solution can be boiled without becoming turbid. If, however, a little nitric acid is added, a yellow precipitate is formed immediately, consisting of basic ceric nitrate; on the addition of more acid the precipitate redissolves. This can be explained as follows: By treating the solution of ceric nitrate with considerable water it becomes hydrolyzed, but the basic salt produced is present in the *hydrosol* state and is changed by the acid into the *hydrogel* form.

Since lanthanum, neodymium, and praseodymium salts do not yield basic salts under these conditions, this property can be used for separating cerium from these metals.

It is characteristic of cerium to form with ammonium nitrate an easily crystallizable salt, ceric ammonium nitrate: $Ce(NO_3)_4 \cdot 2\ NH_4NO_3 \cdot H_2O$.

All ceric salts may be readily reduced by the ordinary reducing agents (alcohol, HI, SO_2, H_2S, HNO_2, H_2O_2, etc.) to cerous salts.

Reactions in the Wet Way

1. **Alkali Hydroxide** or **Ammonia** precipitates yellow, shiny ceric hydroxide, $Ce(OH)_4$. It dissolves in nitric acid giving a red solution but with hydrochloric acid chlorine is evolved and cerous chloride is formed:

$$2\ Ce(OH)_4 + 8\ H^+ + 2\ Cl^- \rightarrow 2\ Ce^{+++} + Cl_2\uparrow + 8\ H_2O$$

Ceric hydroxide is a weak base, and ceric salts are unstable and easily reduced in acid solutions. Ceric chloride is known only in solution, and it decomposes easily like manganic chloride.

Ceric hydroxide dissolves in sulfuric acid giving a mixture of cerous and ceric sulfates. Dry ceric sulfate is known, and crystals of it with four molecules of water can be obtained, but heating in sulfuric acid solutions causes decomposition:

$$4\ Ce(SO_4)_2 + 2\ H_2O \rightarrow 2\ Ce_2(SO_4)_3 + 2\ H_2SO_4 + O_2\uparrow$$

2. **Ammonium Nitrate** in concentrated nitric acid solution gives a relatively insoluble double nitrate, $Ce(NH_4)_2(NO_3)_6$. The other cerite metals form double nitrates much more soluble in nitric acid.

3. **Hydrogen Peroxide** reduces acid solutions of ceric salts:

$$2\ Ce^{++++} + H_2O_2 \rightarrow 2\ Ce^{+++} + 2\ H^+ + O_2\uparrow$$

4. **Oxalic Acid** added to a concentrated solution of a ceric salt at first forms a dirty orange precipitate which gradually becomes yellow and gelatinous as the addition of oxalic acid is continued, and finally becomes crystalline. The precipitate dissolves in a large excess of oxalic acid, but the solution gradually becomes turbid in the cold, or more quickly on heating, since the ceric salt is reduced to cerous salt at the expense of the oxalic acid from which carbon dioxide is evolved. Finally all the cerium will be precipitated as cerous oxalate. (Difference from La, Pr and Nd and the yttrium earths.)

Ammonium Oxalate behaves similarly.

Reactions in the Dry Way

The borax bead is colored dark brown when hot and light yellow to colorless when cold, after being heated in the oxidizing flame. In the reducing flame the bead becomes colorless, although strongly ignited CeO_2 will remain suspended in the bead, giving it a turbid yellowish appearance.

LANTHANUM, La. At. Wt. 138.92, At. No. 57

Density 6.16. M. P. 826°

Lanthanum forms only one oxide,* La_2O_3, which, even after being strongly ignited, dissolves readily in acids. Its salts are colorless and yield no absorption spectrum, so that lanthanum may be distinguished in this way from praseodymium, neodymium, and erbium. The arc spectrum, however, shows characteristic lines in the violet and ultra-violet part. It is the most basic of the cerite earths. The oxide is white when pure and resembles calcium oxide (lime) in its behavior toward water and toward carbon dioxide. The sulfate, $La_2(SO_4)_3 \cdot 9\ H_2O$, is sparingly soluble in water; the *anhydrous* sulfate dissolves much more readily in ice water (cf. p. 562). The presence of phosphoric acid makes these sulfates more soluble; thus cerite when fumed with sulfuric acid will dissolve quite easily in water at the room temperature.

Reactions in the Wet Way

A solution of lanthanum nitrate, $La(NO_3)_3$, should be used.

1. **Alkali Hydroxides** precipitate the white hydroxide, $La(OH)_3$. There is no change to be noticed on treating with oxidizing agents (difference from Ce). $La(OH)_3$ is soluble enough in water to turn red litmus paper blue, and it decomposes ammonium salts on warming with evolution of ammonia. The fused oxide is readily soluble in acids.

2. **HF** precipitates white gelatinous lanthanum fluoride, which eventually becomes crystalline $LaF_3 \cdot 3\ H_2O$; the precipitate is insoluble in an excess of the precipitant and in dilute acid; it is gradually dissolved by strong mineral acids.

3. **Iodine.** — If ammonia is added to a cold, dilute acetic acid solution of a lanthanum salt, and the slimy precipitate is washed with water and then treated with solid iodine, the whole mass gradually assumes a blue color which is similar to that produced by the action of iodine upon starch. The blue color is destroyed by the addition of acids or alkalies.

This property is unreliable as a test for La in rare earth mixtures, because praseodymium gives a bluish violet color under similar conditions and cerium, through atmospheric oxidation, also turns bluish gray to bluish violet.

* H_2O_2 is said to cause the formation of La_2O_5. Cf. *Z. anorg. Chem.*, **21**, 70 (1899).

4. **K_2SO_4** precipitates white, crystalline $La_2(SO_4)_3 \cdot 3K_2SO_4$, insoluble in a concentrated K_2SO_4 solution.

5. **Lanthanum Sulfate,** when anhydrous, dissolves readily in ice-cold water; on warming the concentrated solution to 30° nearly all the lanthanum is precipitated as sparingly soluble $La_2(SO_4)_3 \cdot 9\ H_2O$, which is only one-fourth as soluble as $Ce_2(SO_4)_3$ with 8 and 9 H_2O.

6. **$(NH_4)_2CO_3$** produces a white precipitate slightly soluble in an excess of the reagent (difference from aluminum); after standing some time crystalline lanthanum ammonium carbonate is precipitated.

7. **NH_4OH** and **$(NH_4)_2S$** precipitate a white basic salt which is difficult to filter. The presence of tartaric acid prevents the precipitation (difference from yttrium).

8. **$Na_2S_2O_3$** does not cause precipitation of lanthanum ions.

9. **Oxalic Acid** produces a white crystalline precipitate, insoluble in an excess of the precipitant and in ammonium oxalate, but soluble in dilute mineral acids (difference from Th).

NEODYMIUM, Nd. At. Wt. 144.27, At. No. 60

Density 6.90. M. P. 840°

Salts of this element are separated from the waste of the thorium industry in working up monazite ores by repeated crystallization of the magnesium and manganese double nitrates. The oxide Nd_2O_3 after being ignited has a light blue color when perfectly pure, with a weak, reddish fluorescence. Slight admixture of praseodymium or manganese produces a yellow-brown mixed color.

The salts of neodymium are reddish violet and show a beautiful fluorescence of pink toward blue and violet. This fluorescence is particularly noticeable if a salt, such as the oxalate, is spread out upon white paper and viewed in reflected sunlight. The solution of the nitrate shows in reflected light the following principal absorptions: λ = 677, 578-572, 532-509, 475, 479, 427 mμ.

PRASEODYMIUM, Pr. At. Wt. 140.92, At. No. 59

Density 6.60. M. P. 940°

This element is found in about half as large quantities as neodymium in cerite minerals. In the fractional crystallization of the ammonium-magnesium complex nitrates, the praseodymium is found between lanthanum and neodymium.

The name was given on account of the green colored salts whose absorption spectra show maximums at λ = 597, 592, 481, 469, and 444 mμ.

The oxide Pr_2O_3, from which the salts are derived, is yellow but by heating in oxygen at 300° or by fusing with sodium chlorate it is changed to black PrO_2.

Even small quantities of praseodymium color a mixture of cerite earths cinnamon brown, probably on account of the formation of a solid solution of CeO_2 and PrO_2.

ILLINIUM, Il. At. Wt. 146–148, At. No. 61

The discovery of illinium* has completed the list of the rare earths. Illinium, named after Illinois and the University of Illinois where most of the work on this element has been done, is probably the least abundant of all the elements of this group. It can be detected by x-ray spectra and determined by the magneto-optic method. Its properties are similar to those of other rare earths; the quantities present in monazite residues of the gas-mantle industry or in minerals such as gadolinite are so small that three years of daily fractional precipitations involving many thousand operations were insufficient to produce any considerable quantity of pure illinium salt. As measured by sodium nitrite precipitation, illinium is slightly more basic than yttrium and more basic than samarium. The basicity of the rare earths decreases, as a rule, with rise in atomic number, except in the case of yttrium.

The order is this:

At. No.:	57	59	60	62	61	64	39	66
Symbol:	La	Pr	Nd	Sm	Il	Gd	Y	Dy

SAMARIUM, Sm. At. Wt. 150.43, At. No. 62

Samarium is the least basic member of the cerite earth group and is somewhat similar to terbium of the yttrium earth group. Its salts are colored topaz yellow and are of the trivalent metal type. Its reactions are similar to those of the other members of the group. The double nitrate, according to the general rule given on page 563, is the most soluble and least stable of the group. Samarium solutions show principal absorption bands at λ = 560, 500, 480, 463, 417 mμ, but the bands are much less distinct than the absorption bands of neodymium and praseodymium.

THALLIUM, Tl. At. Wt. 204.39, At. No. 81

Density 11.9. M. P. 302. B. P. 1650°

Occurrence. — Thallium is found in nature very sparingly: in small amount in many varieties of pyrite, and accompanying potassium in carnallite and sylvite, in many lithium micas and in many mineral waters. It replaces the silver to a considerable extent in copper silver selenide, (crookesite, $(Ag,Tl,Cu)_2Se$), and in berzelianite, $(Cu,Ag,Tl)_2Se$. There are no characteristic thallium minerals. The principal source of thallium is the dust from sulfuric acid plants where pyrite containing thallium is used.

Properties. — Metallic thallium reminds one of lead in its color, softness, high density, and low melting point. On bending, it *cries* like tin.

Thallium dissolves readily in nitric and sulfuric acids, but not so readily in hydrochloric acid. It forms two oxides: thallous oxide, Tl_2O, and thallic oxide, Tl_2O_3; both are anhydrides of bases, and from them thallous and thallic salts are derived.

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* Harris, Hopkins, and Yutema, *J. Am. Chem. Soc.*, **48**, 1585 (1926).

A. Thallous Compounds

Thallous compounds are colorless and soluble in water as a rule. The sulfide, chloride, bromide, iodide, and chromate are insoluble in water. Thallous oxide is a dark powder; its aqueous solution reacts alkaline and absorbs carbon dioxide with avidity. Boiling with nitric acid does not oxidize thallous salts, but aqua regia, chlorine, and bromine cause the formation of trivalent thallic salt.

Thallium is like lead in respect to its specific gravity and to the solubility of its halogen compounds; but, on the other hand, it is similar to the alkalies with regard to the solubility and alkaline reaction of the hydroxide and carbonate, and with regard to its forming an insoluble chloroplatinate, an alum, and an insoluble cobaltinitrite.

Reactions in the Wet Way

Use a solution of thallous sulfate for the following reactions:

1. **Alkali Carbonates** cause precipitation only in very concentrated solutions, for thallous carbonate is fairly soluble (100 parts of water dissolve 5 parts of the salt).

2. **Alkali Chromates** precipitate yellow thallous chromate, insoluble in cold nitric or sulfuric acid.

Tl_2CrO_4 is more soluble than $PbCrO_4$. One liter of water at 60° will dissolve 0.3 g of Tl_2CrO_4 but only 0.1 g of $PbCrO_4$.

3. $Al_2(SO_4)_3$. — If a solution of thallous sulfate is treated with aluminum sulfate and the solution is then allowed to crystallize, glistening, colorless octahedrons are obtained of an alum, $TlAl(SO_4)_2 \cdot 12\ H_2O$.

4. **HCl** and **HBr** produce heavy precipitates of white TlCl and pale yellow TlBr. The chloride is appreciably soluble in hot water, the bromide less soluble, and the iodide practically insoluble. The fluoride, on the other hand, is easily dissolved by water.

5. H_2S causes no precipitation from solutions which contain mineral acids; in neutral solutions, thallium is incompletely precipitated as black thallous sulfide, Tl_2S. Tl_2S is readily soluble in mineral acids, but insoluble in acetic acid and alkaline sulfides. It is oxidized readily on standing in the air to thallous sulfate.

6. $H_2[PtCl_6]$ precipitates light yellow thallium chloroplatinate, which is quite insoluble in water; 1 part dissolves in 15,600 parts of water at 15° C and in 1,950 parts of water at 100° C.

7. $K_3[Fe(CN)_6]$ precipitates brown $Tl(OH)_3$ in alkaline solutions:

$$2\ [Fe(CN)_6]^{---} + 3\ OH^- + Tl^+ \rightarrow 2\ [Fe(CN)_6]^{---} + Tl(OH)_3$$

8. **KI** precipitates yellow thallous iodide, TlI, from even dilute solutions. Unlike lead iodide, TlI does not dissolve in cold sodium thiosulfate solution.

TlI is much less soluble than PbI_2. At room temperature, 1 l of water will dissolve 0.61 g of PbI_2 and only 0.08 g of TlI_2. Moreover, an excess of KI makes PbI_2 more soluble because a complex anion, PbI_4^{--}, is formed, but an excess of KI makes TlI less soluble by the common-ion effect.

9. **KOH, NaOH,** or NH_4OH produces no precipitation.

10. $(NH_4)_2S$ precipitates all the thallium as Tl_2S.

11. **Sodium Cobaltinitrite** precipitates light red thallous cobaltinitrite:

$$[Co(NO_2)_6]^{---} + 3\ Tl^+ \rightarrow Tl_3[Co(NO_2)_6]$$

12. **Zinc, Aluminum,** or **Magnesium** precipitates metallic thallium in the form of black, tiny crystals:

$$Zn + 2\ Tl^+ \rightarrow Zn^{++} + 2\ Tl$$

B. Thallic Compounds

Although thallous salts can be oxidized by aqua regia, chlorine, or bromine, the best way to prepare thallic salts is by dissolving thallic oxide in acids.* Thallic compounds can be distinguished from thallous compounds by the ease with which they undergo hydrolysis in aqueous solution. Thus thallic sulfate is decomposed on boiling its aqueous solution into thallic hydroxide and sulfuric acid; the nitrate behaves similarly.

The chloride, $TlCl_3$, is a hygroscopic and not very stable substance; on being heated to 100° C chlorine is evolved with the formation of thallous chloride.

Reactions in the Wet Way

1. **Alkali Acetates** precipitate TlO(OH) on boiling.

2. **Alkali Hydroxide** and **Ammonia** precipitate from solutions of thallic salts, brown thallic hydroxide, $Tl(OH)_3$, which changes to TlO(OH) on standing in the air; it is difficultly soluble in acids and insoluble in an excess of alkali.

3. **Ether.**—Thallic chloride, like $FeCl_3$ and $GaCl_3$, is more soluble in ether-HCl than in water-HCl. These three chlorides can be shaken out of solution in 6 *N* HCl by ether.

4. **HCl** and **Alkali Chromates** do not cause precipitation.

5. H_2S in acid solutions causes reduction with precipitation of sulfur:

$$H_2S + Tl^{+++} \rightarrow Tl^+ + 2\ H^+ + S$$

If the acid is neutralized, thallous sulfide precipitates.

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* Tl_2O_3 is not attacked in the cold by concentrated sulfuric acid, but is dissolved on warming. The hydrated oxide, TlO(OH), is much more soluble.

Shaking with mercury reduces a solution of thallic chloride to thallous chloride:

$$TlCl_3 + 2\,Hg \rightarrow Hg_2Cl_2 + TlCl$$

Thallic salts are also reduced by sulfurous acid, and Tl_2SO_4, unlike $PbSO_4$, is soluble in water.

6. **KI** precipitates thallous iodide with deposition of iodine:

$$3\,I^- + Tl^{+++} \rightarrow TlI + I_2$$

Reactions in the Dry Way

Thallium salts color the non-luminous gas flame a beautiful emerald green. The thallium spectrum consists of a green line at **535.0** mμ, nearly coincident with the green barium line at 534.7 mμ.

INDIUM, In. At. Wt. 114.76, At. No. 49

Density 7.3. M. P. 155°

Indium was discovered in zinc ores and has also been found associated with tungsten. The free element is a white, lustrous metal resembling platinum in appearance. It is very soft and ductile and leaves a mark on paper. It is oxidized slowly in contact with air but less readily than zinc. The metal dissolves in dilute hydrochloric and sulfuric acids with liberation of hydrogen and formation of trivalent indium ions:

$$2\,In + 6\,H^+ \rightarrow 2\,In^{+++} + 3\,H_2\uparrow$$

Nitric acid dissolves it readily, but with sulfuric acid the anhydrous salt separates out.

Indium forms three chlorides, InCl, $InCl_2$, and $InCl_3$, but only the salts of the trivalent metal are stable in aqueous solutions. Indium oxide, In_2O_3, is pale yellow when cold and reddish brown when hot. Heating it in hydrogen gas or with carbon gives reduction to metal. The ignited oxide dissolves slowly in cold acids but more readily in hot, dilute acids. Indium salts are colorless; the sulfate, nitrate, and chloride dissolve in water.

Reactions in the Wet Way

1. **Alkali Acetate** added to a solution until p_H = about 5.3 does not cause the precipitation of small quantities of indium basic salt from pure $InCl_3$ solutions, but if considerable ferric iron is present, the precipitation of the indium as basic salt is practically complete.

2. **$BaCO_3$** precipitates a basic salt even in the cold (difference from Zn, Mn, Co, Ni, and Fe).

3. **H_2S** in slightly acid solutions gives a yellow precipitate of indium sulfide:

$$2\,In^{+++} + 3\,H_2S \rightarrow In_2S_3 + 6\,H^+$$

The precipitate forms in the presence of 6-normal acetic acid but does not form in 0.3-normal solution of mineral acid.

4. **KOH, NaOH,** and **NH_4OH** precipitate white, gelatinous indium hydroxide:

$$In^{+++} + 3\ OH^- \rightarrow In(OH)_3$$

The precipitate resembles aluminum hydroxide in appearance and behavior. Tartaric acid prevents its formation. It dissolves in excess of sodium or potassium hydroxide solution, but the liquid becomes turbid on standing, and boiling with ammonium chloride causes the reprecipitation of the hydroxide.

Na_2O_2 also precipitates $In(OH)_3$. The precipitate is soluble in HF and can be distinguished from $Ti(OH)_4$ and $Zr(OH)_4$ by partially neutralizing the HF solution with NH_4OH and introducing H_2S; yellow in In_2S_3 precipitates. If considerable rare earth element is present (*e.g.*, Ce), the $In(OH)_3$ often fails to dissolve in HF. Then, to remove In from the rare earths it is best to decompose the fluorides by fuming with H_2SO_4, precipitate $In(OH)_3$ with rare earth hydroxides by adding NH_4OH, dissolve out the $In(OH)_3$ with 6 *N* $HC_2H_3O_2$, and precipitate In_2S_3 with H_2S.

5. **$K_3[Fe(CN)_6]$, KCNS,** and **$K_2Cr_2O_7$** give no precipitation. **K_2CrO_4** produces a yellow precipitate.

6. **$K_4[Fe(CN)_6]$** gives a white precipitate of indium ferrocyanide.

7. **Na_2CO_3, K_2CO_3,** and **$(NH_4)_2CO_3$** precipitate white, gelatinous $In_2(CO_3)_3$. It dissolves in an excess of cold ammonium carbonate solution but reprecipitates on boiling.

8. **Na_2HPO_4** gives a white, voluminous precipitate.

Indium phosphate is not usually precipitated by Na_2HPO_4 in acid solutions but in the presence of zirconium and titanium it is likely to be carried down with $Zr(HPO_4)_2$ and $Ti(HPO_4)_2$ making it necessary to remove indium before testing for Zr or Ti with Na_2HPO_4.

9. **$(NH_4)_2C_2O_4$** precipitates white, crystalline indium oxalate from concentrated solutions.

10. **$(NH_4)_2S$** gives a white sulfide precipitate. By boiling the yellow sulfide with yellow ammonium sulfide, it is changed to white sulfide and dissolves to some extent; on cooling, a white voluminous sulfide precipitate is formed. It is not quite clear just what formulas should be assigned to the white and yellow sulfide precipitates.

11. **Zinc** precipitates indium as white, lustrous flakes.

Reactions in the Dry Way

Heated on charcoal, the surface of the charcoal is given a lustrous metallic coating. Indium salts color the flame a peculiar bluish violet. In the spectrum two distinct blue lines are seen at 451.1 mμ and 410.1 mμ.

GALLIUM, Ga. At. Wt. 69.72, At. No. 31

Density 5.96. M. P. 301°

Gallium is of quite common occurrence in small quantities. It is found in many samples of sphalerite and in bauxites as well as in other minerals. It is a hard, white metal which is not very ductile and is not easily oxidized.

Hydrochloric acid, potassium hydroxide, and ammonia dissolve gallium with evolution of hydrogen gas:

$$2\ Ga + 6\ H^+ \rightarrow 2\ Ga^{+++} + 3\ H_2\uparrow$$

$$2\ Ga + 2\ OH^- \rightarrow 2\ [GaO_2]^- + H_2\uparrow$$

$$2\ Ga + 6\ H_2O + 8\ NH_3 \rightarrow 2\ [Ga(NH_3)_4]^{+++} + 3\ H_2\uparrow + 6\ OH^-$$

The metal is passive to cold nitric acid but on heating it dissolves and red vapors are evolved.

$$Ga + 6\ HNO_3 \rightarrow Ga(NO_3)_3 + 3\ H_2O + 3\ NO_2\uparrow$$

Gallium forms bivalent gallous salts and trivalent gallic salts. The gallous compounds are unstable and easily oxidized. Gallic oxide, Ga_2O_3, and its hydroxide, $Ga(OH)_3$, are white. Gallic salts are colorless or white. Gallic chloride is a colorless, hygroscopic substance which melts at 75° and boils at 215–220°. Evaporation of gallic chloride solutions causes volatilization of gallic chloride, but there is no loss of gallium if sulfuric acid is present.

Reactions in the Wet Way

1. **Alkali Acetate** added to reduce the acidity to p_H = about 5.3 causes the precipitation of a basic salt on boiling. The precipitation is incomplete if the solution is much more acid or basic.

2. **Ammonium Sulfide** gives a precipitate only when another insoluble sulfide is formed.

3. **$BaCO_3$** causes complete precipitation in the cold.

4. **Ether** dissolves out $GaCl_3$ from aqueous hydrochloric acid solution. $FeCl_3$ and $TlCl_3$ are also dissolved by ether. If the ethereal solution is diluted with water and shaken with mercury to reduce the iron and thallium, another shaking with ether dissolves out $GaCl_3$ alone.

5. **H_2S** gives no precipitate in dilute acid solutions. There is likelihood, however, of small quantities of gallium being dragged down in the copper group.

6. **$K_4Fe(CN)_6$** in the presence of dilute acid precipitates a white or bluish white precipitate of gallium ferrocyanide.

7. Na_2CO_3 and $(NH_4)_2CO_3$ give white precipitates. Excess of ammonium carbonate causes the precipitate to redissolve.

8. **NaOH, KOH,** and NH_4OH precipitate white, flocculent gallic hydroxide:

$$Ga^{+++} + 3\ OH^- \rightarrow Ga(OH)_3$$

readily soluble in an excess of precipitant:

$$Ga(OH)_3 + 3\ OH^- \rightarrow [GaO_3]^{---} + 3\ H_2O$$

Boiling the ammoniacal solution causes slow reprecipitation of the hydroxide. Tartaric acid prevents precipitation by ammonia.

Reactions in the Dry Way

Gallium compounds give two violet lines in the spark spectrum between the G and H lines at 417.0 and 403 mμ. With the Bunsen flame only one faint line is seen.

VANADIUM, V. At. Wt. 50.95, At. No. 23

Density 5.82. M. P. 1720°. B. P. about 3400°

Occurrence. —Vanadinite, $Pb_5(VO_4)_3Cl$; carnotite;* mottramite, $(Cu,Pb)_5V_2O_{10} \cdot 2H_2O$; many clays and in almost all granite.

Properties. — Metallic vanadium is silver-white or pale gray. It is often obtained from its ores in the form of ferro-vanadium, which is used in steel making. Vanadium is found in various metallurgical products and sometimes in caustic soda. The metal has strong reducing power, is soluble in hydrochloric acid, and is harder than any other metal. The name comes from *Vanadis*, a Scandinavian goddess.

Vanadium, like nitrogen, forms five oxides: V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5.

The first three of these oxides are basic anhydrides. Compounds representing these valences of vanadium are not encountered in qualitative analysis except, to some extent, in the tests for vanadium with strong reducing agents. Vanadous oxide, V_2O_2, is dark gray and lustrous. It is insoluble in water but dissolves in dilute acids to form blue solutions which, because of their strong reducing powers, decolorize organic dyestuffs.

Vanadic oxide, V_2O_3, is black, insoluble in acids (except hydrofluoric and nitric acids) and in alkali hydroxide solutions. By ignition in hydrogen it is not reduced, but on standing in the air it slowly changes into vanadyl oxide, V_2O_4. Acid solutions containing trivalent vanadic salts are green. The oxides V_2O_4 and V_2O_5 represent the types of vanadium compounds usually encountered in analytical chemistry.

Vanadyl oxide, V_2O_4 (also called vanadium tetroxide), is the anhydride of hypovanadic acid, $V_2O_3(OH)_4$. This compound is an amphoteric substance and forms salts with both acids and bases. V_2O_4 itself is a blue powder, soluble in concentrated

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*According to Friedel and Cumenge, carnotite contains 18 per cent V_2O_5 and 55 per cent UO_3, as well as K, Ca, Ba, H, As, and P. (Cf. Hillebrand and Ransome, *Am. J. Sci.*, **10**, 138.)

acids, forming blue divanadyl salts:

$$V_2O_4 + 2\ H_2SO_4 \rightarrow V_2O_2(SO_4)_2 + 2\ H_2O$$

If the solution of divanadyl sulfate is treated with sodium carbonate or ammonia (avoiding excess), hypovanadic acid separates out as a grayish white precipitate, which, like the anhydride, is soluble in acids with blue color and in alkalies with a brown color. The alkali hypovanadates correspond to the formulas $Na_2V_2O_5$ and $Na_4V_4O_9$. Hypovanadates of other metals are for the most part insoluble in water and such precipitates may form when an acid solution containing vanadium is neutralized. The divanadyl compounds are readily formed by reducing solutions of the pentoxide in mineral acids with sulfurous acid (cf. p. 582), and serve, on account of their blue color, for the detection of vanadium.

Vanadium pentoxide, V_2O_5, is the anhydride of vanadic acid and is an orange-red, crystalline mass, which is readily fusible but non-volatile. It is only slightly soluble in water, forming a faintly acid, yellow solution, but readily soluble in concentrated solutions of caustic alkalies, forming vanadates. By heating with nitric acid or aqua regia, as well as by fusion with an alkaline oxidizing flux, all the lower oxides are changed into vanadium pentoxide, V_2O_5, or one of its salts.

Like phosphoric acid, vanadic acid exists in the form of meta-, pyro-, ortho-, and poly- compounds, of which the meta-compounds are the most stable and the ortho-compounds the least so. Thus an aqueous solution of potassium or sodium ortho-vanadate is hydrolyzed, even in the cold, into the pyro-salt and alkali hydroxide,

$$2\ Na_3VO_4 + H_2O \rightleftarrows Na_4V_2O_7 + 2\ NaOH$$

and on boiling, the meta-salt is formed:

$$Na_4V_2O_7 + H_2O \rightleftarrows 2\ NaVO_3 + 2\ NaOH$$

The meta-, pyro-, and ortho-salts of the alkalies are colorless or slightly yellow, while the polyvanadates, *e.g.*, the tetra- and hexavanadates, are intensely orange or reddish. Thus the colorless or light-yellow solutions of the ortho-, meta-, and pyro-vanadates are colored intensely orange on the addition of acid.

Strong acids dissolve vanadium pentoxide forming red or yellow solutions. Such solutions probably contain the quinquevalent vanadium in the cation as VO_2^+, VO^{+++} and possibly a little V^{+++++}. The equilibria between the vanadium in cations and in anions are illustrated by the following equations:

$$V_2O_7^{=\,=} + 6\ H^+ \rightleftarrows 2\ VO_2^+ + 3\ H_2O$$
$$2\ VO_2^+ + 6\ OH^- \rightleftarrows V_2O_7^{=\,=} + 3\ H_2O$$
$$V_2O_7^{=\,=} + 10\ H^+ \rightleftarrows 2\ VO^{+++} + 5\ H_2O$$
$$V_2O_7^{=\,=} + 14\ H^+ \rightleftarrows 2\ V^{+++++} + 7\ H_2O$$
$$2\ V^{+++++} + 14\ OH^- \rightleftarrows V_2O_7^{=\,=} + 7\ H_2O$$

In acid solutions, the vanadium is easily reduced to blue vanadyl salt, and the change takes place slowly on standing or by evaporating the solution in hydrochloric acid.

Besides the above types of vanadium compounds, this element exists as pervanadic acid, HVO_4, formed by the addition of hydrogen peroxide to the acid solution of a vanadate.

The reactions of quadrivalent and quinquevalent vanadium will be considered together; the other compounds are not common enough to make it necessary to describe their characteristic reactions.

Reactions in the Wet Way

1. **Barium Chloride,** but not strontium and calcium chloride, **Silver Nitrate** and **Lead Acetate** give yellow precipitates which become white on standing or on heating.

2. **Ferric Chloride and Dimethylglyoxime.** — The reversible reaction,

$$V_2O_2^{++++} + 2\ Fe^{+++} + 4\ H_2O \rightleftarrows 2\ HVO_3 + 2\ Fe^{++} + 3\ H^+$$

takes place from left to right in alkaline solutions and from right to left in acid solutions, as might be expected from the mass-action law. A sensitive test for Fe^{++} is the dimethylglyoxime reaction. Since vanadic acid and vanadates are easily reduced to vanadyl salt by heating with concentrated HCl, the test for Fe^{++} with the glyoxime can be used to indicate the presence of vanadium.

Place 1 drop of the alkaline solution to be tested for vanadate in a small crucible, add 2 drops of concentrated HCl, and evaporate nearly to dryness. Pour the residual solution upon a piece of filter paper; add 1 drop of 1 per cent $FeCl_3$ solution and 3 drops of 1 per cent dimethylglyoxime solution. As little as 1 γ of vanadium will give a cherry-red or brown color. A blank test must be run on the reagent, and other reducing agents must be absent; the heating with concentrated acid usually accomplishes the removal of reducing agents.

3. **8-Hydroxyquinoline,** C_9H_6NOH (cf. pp. 192, 272), reacts with vanadates in the presence of acetic acid to give a yellow precipitate of $(C_9H_6NOH)_2 \cdot H_2V_4O_{11}$ which changes to very dark blue $(C_9H_6NOH)_4V_2O_3$ when heated. Molybdenum, tungsten, and titanium give similar tests. If the solution used has been prepared by fusing or boiling with Na_2CO_3, the tungstic and molybdic acids can be removed by making the solution acid with acetic acid and adding barium acetate solution. Ferric iron also gives a brown precipitate with the reagent and interferes. It can be removed by adding a little strong sodium hydroxide solution, filtering off the ferric hydroxide precipitate, and testing the filtrate for vanadium.

Procedure. — Place a few drops of the solution in a small test tube, make acid with a few drops of acetic acid, and add a drop or two of 2.5 per cent solution of "oxine" in 6 per cent acetic acid. Shake the solution with a little chloroform; as little as 0.1 of vanadium will give a red or brownish violet color to the chloroform.

4. **H_2O_2.** — If an acid solution of a vanadate is treated with a few drops of H_2O_2 and shaken, the solution becomes colored reddish brown owing to the formation of pervanadic acid, HVO_4, or vanadium peroxide sulfate* insoluble in ether. This is a very delicate reaction if the solution is 2–6 normal in HNO_3 or H_2SO_4 and an excess of peroxide is avoided.

This reaction can be used in a sensitive spot test which will detect 2.5 γ of vanadium in 1 drop of solution. Mix a drop of the solution with 1 drop of 4 *N* H_2SO_4. After a few minutes add 1–2 drops of 1 per cent H_2O_2; a reddish coloration will appear if vanadium is present.

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* Myer and Pawleta, *Z. anal. Chem.*, **69**, 15 (1926).

5. **H_2S** gives no precipitation of sulfide when added to an acid solution of either vanadyl salt or vanadic acid. Like other reducing agents (SO_2, HCl, formic acid, Fe^{++}, oxalic acid, tartaric acid, ethyl alcohol, sugar, etc.) it reduces vanadic acid to blue vanadyl salt. The reaction takes place slowly in the cold but more rapidly on heating:

$$2\ H_3VO_4 + H_2S + 4\ H^+ \rightarrow V_2O_2^{++++} + 6\ H_2O + S$$
$$2\ H_3VO_4 + 2\ Fe^{++} + 6\ H^+ \rightarrow V_2O_2^{++++} + 2\ Fe^{+++} + 6\ H_2O$$
$$2\ H_3VO_4 + HCHO_2 + 4\ H^+ \rightarrow V_2O_2^{++++} + CO_2 + 6\ H_2O$$

HI carries the reduction further forming green, trivalent vanadium salt:

$$H_3VO_4 + 2\ HI + 3\ HCl \rightarrow VCl_3 + 4\ H_2O + I_2$$

The green color is noticed after the iodine has been boiled off.

Metals, such as Zn, Al, and Cd, cause still further reduction of vanadic acid, so that the solution turns at first blue (vanadyl salt), then green (trivalent vanadium), and finally violet or lavender blue (bivalent vanadium). Ammonium hydroxide added to the fully reduced solution gives a brown precipitate which oxidizes easily.

6. **Mercurous Nitrate** precipitates white mercurous vanadate from neutral solutions of a vanadate; the precipitate is soluble in nitric acid.

7. **$NaHCO_3$** gives no precipitate if pure vanadium is present. If the solution contains uranium, uranyl ammonium vanadate, $UO_2NH_4VO_4$, may precipitate.

8. **NH_4Cl.** — If a piece of solid ammonium chloride is added to a solution of an alkali vanadate, colorless ammonium metavanadate separates out,

$$Na_4V_2O_7 + 4\ NH_4Cl \rightarrow 2\ NH_4VO_3 + 2\ NH_3 + H_2O + 4\ NaCl$$

difficultly soluble in a concentrated solution of ammonium chloride.

9. **NH_4OH** added to a cold, green, acid solution of a vanadate, containing some vanadium in the form of cations, causes the color to become yellow. After the solution has been neutralized, no further change is produced if the solution contains none but alkali cations. In the presence of other cations, however, the vanadate ion behaves like phosphate ion toward ammonia; vanadates of ferric iron, aluminum, uranium, and barium are likely to be precipitated by ammonia.

NH_4OH added to a solution of a vanadyl salt precipitates dark gray hypovanadic acid:

$$V_2O_2Cl_4 + 4\ NH_4OH \rightarrow 4\ NH_4Cl + V_2O_2(OH)_4$$

The precipitation is not quantitative, and small quantities of vanadium may remain in solution when the vanadyl salt is alone present. If, however, an excess of ferric chloride is added to the solution, the vanadium is quantitatively precipitated upon the addition of ammonia. This is true both of vanadic acid and of vana-

dyl salt, ferric vanadate and ferric hypovanadate being precipitated with the ferric hydroxide. Instead of ferric chloride, an aluminum or uranium salt may be used for the same purpose.

Sodium Hydroxide added to an acid solution of quinquevalent vanadium gives a brown precipitate soluble in an excess of the base and giving a yellowish green solution. Na_2O_2 in alkaline solution has no further effect.

10. $(NH_4)_2S$ produces no precipitation, but causes the solution to turn brown, owing to the formation of thio-salts.

If hydrogen sulfide is conducted into a strongly ammoniacal solution of a vanadate or hypovanadate, the solution at first turns yellowish red, but the color slowly deepens until eventually a characteristic, brilliant, violet-red color is obtained when the solution has become saturated with H_2S. Ammonium salts interfere somewhat with this test, but their influence is overcome by the addition of a large excess of ammonia. The red color is probably caused by the formation of ammonium thiovanadate. As little as 0.2 mg of vanadium can be recognized by the red color.

The addition of acid to the red solution produces a black precipitate of V_2S_4 or V_2S_5. The precipitation is not quantitative; the filtrate is always colored blue and contains detectable amounts of vanadyl salts. The precipitate is soluble in alkali hydroxides, alkali carbonates, and alkali sulfides, forming a brown solution. If the sulfide is heated to 500–600° in an atmosphere of H_2S, black V_2S_3 is formed, insoluble in concentrated hydrochloric acid. V_2S_3 dissolves in aqua regia forming vanadic acid, but by evaporating the solution with an excess of HCl, blue vanadyl salt is formed.

Molybdenum gives a similar red color, if it was not completely removed by previous treatment with hydrogen sulfide in acid solution, and obscures the above test or may be mistaken for vanadium.

Ammonium sulfide added to an acid solution of quinquevalent vanadium precipitates brown V_2S_5, slowly dissolved by an excess of the reagent.

11. **Oxidizing Agents** convert divanadyl compounds into vanadic acid. The oxidation may be effected by bromine in hydrochloric acid solution,

$$[V_2O_2]^{++++} + Br_2 + 6\,H_2O \rightarrow 2\,VO_4^{---} + 2\,Br^- + 12\,H^+$$

by dilute potassium permanganate in hot, very dilute sulfuric acid solution,

$$5\,[V_2O_2]^{++++} + 2\,MnO_4^- + 22\,H_2O \rightarrow 10\,VO_4^{---} + 2\,Mn^{++} + 44\,H^+$$

or by sodium peroxide in alkaline solution:

$$[V_2O_2]^{++++} + Na_2O_2 + 8\,OH^- \rightarrow 2\,VO_4^{---} + 2\,Na^+ + 4\,H_2O$$

Chromium, aluminum, vanadium, and uranium may be separated from iron, nickel, cobalt, and manganese by means of this reaction; the chromate is left in solution as sodium chromate, Na_2CrO_4, the aluminum as sodium aluminate, $NaAlO_2$, the vanadium as sodium vanadate, Na_3VO_4, the uranium as sodium peruranate, and the zinc as sodium zincate, Na_2ZnO_2; while the iron is precipitated as $Fe(OH)_3$, the nickel as $Ni(OH)_2$, the cobalt as $Co(OH)_3$, and the manganese as hydrated MnO_2.

12. $Pb(C_2H_3O_2)_2$ precipitates vanadic acid quantitatively as yellow lead vanadate:

$$3\,Pb^{++} + 2\,VO_4^{---} \rightarrow Pb_3(VO_4)_2$$

This precipitate, however, is more soluble in dilute nitric acid than lead chromate is, and it is possible to separate chromic acid from vanadic acid by treating the solution of the two acids with lead nitrate in dilute nitric acid solution; under the proper conditions all but a fraction of a milligram of the chromium is precipitated and 100 mg of vanadium yields no precipitate.* The vanadium can be detected in the filtrate by the H_2O_2 test.

13. **Potassium Ferrocyanide** added to an acid solution of quinquevalent vanadium gives a green, flocculent precipitate of vanadium ferrocyanide. The precipitate is insoluble in 12 per cent H_2SO_4.

14. **Uranyl Salts** added to an ammoniacal, or slightly acid, solution containing ammonium acetate give a precipitate of uranyl ammonium vanadate $(UO_2)NH_4VO_4 \cdot H_2O$. By means of this reaction vanadate ions can be separated from alkali, alkaline earth, manganese, zinc, and copper ions. The precipitate is much more soluble than $UO_2NH_4PO_4$.

15. To distinguish between ortho- and metavanadates, the following reactions serve:

Copper salts give a bluish green, pulverulent precipitate with metavanadates and an apple-green precipitate with orthovanadates. Lead salts give a white precipitate with orthovanadates, and silver salts give an orange-red precipitate with orthovanadates.

Reactions in the Dry Way

The borax bead is colorless in the oxidizing flame if slightly saturated with the vanadium compound, yellow if strongly saturated, and green in the reducing flame.

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* Neutralize the solution exactly with NaOH, add 2 ml of HNO_3 (density 1.20) and an excess of 20 per cent $(PbNO_3)_2$ solution.

ACIDIC GROUP OF THE EARTH ACIDS

TUNGSTEN, TANTALUM, COLUMBIUM

These three metals are classed together in a separate group because they do not form water-soluble salts with the common acids used as solvents, and therefore do not accompany the other metals in solution in the systematic procedure of qualitative analysis described in Part IV of this book. In that respect they resemble silicon, which is removed from the solution as silicic acid prior to precipitation of the analytical groups.

Tungsten, tantalum, and columbium form acid anhydrides, WO_3, Ta_2O_5, Cb_2O_5, which, like silicic acid, react with alkali hydroxides, giving soluble tungstates, tantalates, and columbates. Unlike silicic acid, however, they also form soluble complex compounds with oxalic, tartaric, and other organic hydroxy-acids.

Of the three metallic acids, tungstic acid stands by itself, being a fairly strong acid forming well-defined stable salts akin to the molybdates. Tantalic and columbic acids, on the other hand, are very weak acids (especially the former), bearing a distinct resemblance to antimonic acid.

TUNGSTEN, W. At. Wt. 184.0, At. No. 74

Density 19.1. M. P. 3400°

Occurrence. — Tungsten is not very often found in nature, but there are a number of well-crystallizing tungsten minerals, such as the minerals of the Scheelite group: scheelite, $CaWO_4$; cuproscheelite, $(Ca,Cu)WO_4$; reinite, $FeWO_4$; stolzite, $PbWO_4$. These minerals all crystallize in the tetragonal system and form with powellite, $CaMoO_4$, and wulfenite, $PbMoO_4$, a very interesting isomorphous group. Another isomorphous group, which consists of minerals crystallizing in the monoclinic system, is formed by hübernite, $MnWO_4$; wolframite, $(Mn,Fe)WO_4$; and ferberite, $FeWO_4$. The most important tungsten mineral is wolframite, which is usually contaminated by small amounts of silicic, tantalic, and columbic acids. Tungsten is used in the form of thin metallic filaments in incandescent electric lamps. Ferro-tungsten is used for making self-hardening or alloy steels. Tungsten forms two oxides, WO_2 and WO_3.

Properties. — WO_2 is a brown powder, readily obtained by heating WO_3 to dull redness in a stream of hydrogen. It is pyrophoric and must, therefore, be cooled in a stream of hydrogen before it is allowed to come into contact with the air. By igniting strongly in a stream of hydrogen, metallic tungsten is obtained, which is stable in the air. This behavior is important and is taken advantage of in the quantitative determination of tungsten.

WO_3 is an acid anhydride obtained by the ignition of tungstic acid or of ammonium or mercurous tungstates, or by the oxidation of the dioxide on heating in the air.

The trioxide is a canary-yellow powder, insoluble in water and dilute acids, and only slightly soluble in concentrated hydrochloric and hydrofluoric acids. It dissolves readily by warming with potassium or sodium hydroxides, and less readily in ammonia.

It is most easily dissolved by fusing with sodium carbonate, sodium tungstate being formed:

$$WO_3 + Na_2CO_3 \rightarrow Na_2WO_4 + CO_2\uparrow$$

It is changed to potassium tungstate by fusing with potassium pyrosulfate:

$$WO_3 + K_2S_2O_7 \rightarrow K_2WO_4 + 2\,SO_3\uparrow$$

If the product of this last fusion is treated with water, usually none of the tungsten goes into solution, because if an excess of potassium pyrosulfate is present (as is usual) it reacts with the potassium tungstate, forming free tungstic acid:

$$K_2WO_4 + K_2S_2O_7 + H_2O \rightarrow 2\,K_2SO_4 + H_2WO_4$$

If not enough pyrosulfate remains to complete the above decomposition, some of the tungsten will be dissolved, but never all of it. If a little sulfuric acid is added to the water, none of the tungsten will go into solution. This property enables one to separate tungsten from titanium. If ammonium carbonate is added, all the tungsten dissolves, which enables us to separate tungstic from silicic acid.

Reactions in the Wet Way

A solution of sodium tungstate should be used.

1. **Acids**, HCl, HNO_3, H_2SO_4, produce, in the cold, a white, amorphous precipitate of hydrated tungstic acid, $H_2WO_4 \cdot H_2O$.* By boiling the solution, the yellow anhydrous acid H_2WO_4 is obtained, insoluble in dilute acids, but soluble to an appreciable extent in concentrated hydrochloric acid.

Tungstic acid must always be washed with water which contains acid or a dissolved salt, as otherwise tungstic acid will form a pseudo-solution with pure water, so that a turbid filtrate will be obtained (cf. pp. 65, 131, and 189).

Phosphoric acid behaves differently from the other mineral acids toward solutions of the alkali tungstates; it produces a white precipitate soluble in an excess of phosphoric acid; a complex phosphotungstic acid is formed, *e.g.*, $Na_3PO_4 \cdot 12\,WO_3$. If the solution of an alkali tungstate is boiled with free tungstic acid, the latter gradually goes into solution, forming a metatungstate:

$$Na_2WO_4 + 3\,WO_3 \rightarrow Na_2W_4O_{13}$$

Mineral acids cause no precipitation in solutions of metatungstates. If the solution is boiled with an excess of acid, the soluble metatungstic acid is gradually changed to insoluble, ordinary tungstic acid, which is then precipitated. The addition of cinchonine hydrochloride greatly hastens the formation of insoluble tungstic acid in acid solutions.

2. Organic **acids** (citric, tartaric, etc.) form complex ions with tungstic acid and prevent its precipitation.

* The presence of tartaric acid prevents the precipitation.

3. **Ferrous Sulfate** gives a yellowish brown precipitate and the precipitate is not turned blue by acid (cf. molybdenum).

4. H_2S produces no precipitation in acid solutions.

5. **Lead Acetate, barium chloride,** and **silver nitrate** also precipitate white tungstates from neutral solutions.

6. **Mercurous Nitrate** precipitates white mercurous tungstate from neutral solutions.

7. $(NH_4)_2S$ gives no precipitation in a solution of an alkali tungstate, but if the solution is afterward acidified, light-brown tungsten trisulfide, WS_3, is precipitated, which has the property of forming colloidal solutions with pure water, but is insoluble in hydrochloric acid. The precipitate dissolves in ammonium sulfide.

8. **Potassium Ferrocyanide** and a little acid give a brownish red solution and a precipitate of the same color.

9. **Reducing Agents.** — If the solution of an alkali tungstate is treated with HCl and zinc, the tungstic acid at first precipitated by the HCl is soon turned to a beautiful blue color, owing to the formation of WCl_5.

$SnCl_2$ produces a yellow coloration at first, but on adding HCl and warming, a beautiful blue precipitate is obtained. This is one of the most sensitive tests for tungstic acid.

Reactions in the Dry Way

The salt of phosphorus bead is colorless in the oxidizing flame, and blue in the reducing flame, becoming blood-red on the addition of a little $FeSO_4$.

TANTALUM, Ta. At. Wt. 180.88. At. No. 73

Density 16.6. M. P. 2800°

COLUMBIUM, Cb.* At. Wt. 92.91. At. No. 41

Density 7.37. M. P. 1950°

These two rare elements belong to the fifth group of the periodic system, and accordingly form pentoxides of the formula R_2O_5; these are the anhydrides of tantalic and columbic acids. The time-honored, generic term "earth acids" is used to denote the two acids, either singly or in admixture. The two elements always accompany each other, not only in their minerals but also in all but a very few chemical operations, so that their separation from one another can be accomplished only by processes of fractionation. Their separation from other elements is complicated by the fact that, unlike most metals, they do not form water-soluble simple salts, hence solution must be achieved by conversion of the earth acids into complex compounds.

* Also called niobium, Nb.

Occurrence. — The commonest earth-acid mineral is columbite (or niobite), a compound of the hypothetical columbic acid, $HCbO_3$, with ferrous oxide: $Fe(CbO_3)_2$, or $FeO \cdot Cb_2O_5$. Tantalum is always present, replacing part of the columbium, while manganese replaces part of the iron; hence the general formula for the mineral is $(Fe,Mn)O \cdot (Cb,Ta)_2O_5$. With increasing tantalum content the density rises from about 5 to beyond 7, and the mineral is designated as tantalite. This is a rare and valuable ore.

The earth acids further occur in a number of very rare minerals in which they are combined with titania, thoria, yttria earths, and uranium oxide; such as yttrotantalite, samarskite, fergusonite, and euxenite. Tantalic acid is also found in monazite, $(Ce,La,Nd,Pr)PO_4$, replacing a subordinate part of the phosphoric acid.

The minerals of the earth acids are decomposed by fusion with alkali bisulfate; extraction of the melt with water yields an insoluble residue of impure earth acid, formed by hydrolysis of the alkali salt. If the extraction is carried out with ammonium tartrate or oxalate, the resulting solution contains the earth acids in the form of their tartaro- or oxalo- complexes. By fusing the minerals with potassium carbonate and extracting with water, solutions containing potassium hexatantalate, $K_8Ta_6O_{19}$, and hexacolumbate, $K_8Cb_6O_{19}$, are obtained.

Properties. — On account of the constant association and close resemblance of tantalum and columbium, the study of these elements is much facilitated if we consider them together.

(*a*) Tantalum is a white metal which is tough, malleable, and ductile, unaltered in the air at ordinary temperature, and unattacked by all acids except hydrofluoric; it is soluble in a mixture of hydrofluoric and nitric acids probably forming H_2TaF_7 or H_2TaF_5O which yield Ta_2O_5 by hydrolysis. At high temperature it readily combines with oxygen, hydrogen, and nitrogen, forming the pentoxide, hydride, and nitride respectively. Columbium closely resembles tantalum in its chemical properties; it has not yet found any application in the arts.

(*b*) The pentoxides are pure white powders. Tantalic oxide remains white on ignition; columbic oxide becomes yellow when heated and returns to its original color on cooling. The oxides dissolve in molten alkali bisulfate; extraction of the melt with water leaves the hydrated earth acids as an insoluble white residue. This retains an indefinite amount of adsorbed sulfuric acid. The bisulfate melt is soluble in ammonium oxalate or tartrate solution.

(*c*) The pentoxides dissolve in molten potassium carbonate, with disengagement of carbon dioxide and formation of water-soluble potassium tantalate and columbate, $K_8Ta_6O_{19}$ and $K_8Cb_6O_{19}$. These salts are known as "hexa-" salts, but since this term is somewhat misleading, they are sometimes designated as 4 : 3 salts, thus indicating the ratio of K_2O to Ta_2O_5 or Cb_2O_5 in the molecule. Thus $K_8Ta_6O_{19}$ can be written $4\ K_2O \cdot 3\ Ta_2O_5$. When the solution of the potassium salts is saturated with solid sodium chloride or nitrate, white crystalline precipitates are formed. These have the composition $4\ Na_2O \cdot 3\ Ta_2O_5$ and $7\ Na_2O \cdot 6\ Cb_2O_5$. The 4 : 3 *sodium* columbate appears to be incapable of existence.

(*d*) The hydrated earth acids separate as white, flocculent precipitates when solutions of alkali tantalate or columbate are acidified with acetic or mineral acids. No definite formula can be assigned to the hydrated acids: they consist of the pentoxides in combination with a variable amount of water. On ignition, they furnish the pentoxides. They are soluble in hydrofluoric, as well as in phosphoric acid. The phosphoric acid solution of columbic acid is reducible to a colored lower oxide; that of tantalic acid does not undergo reduction.

(*e*) The precipitated earth acids are capable of adsorbing tannic acid. When a solution of this reagent is added to the suspension of the precipitated earth acid, the formation of the adsorption complex is indicated by a change of color, the tantalum precipitate turning pale yellow and the columbium precipitate orange-red. From the qualitative diagnostic, as well as from the quantitative point of view, tannin is the most important reagent in earth-acid analysis.

The tannin adsorption complexes of the earth acids are also obtained when solutions of their oxalo- or tartaro- complexes are treated with tannin. The tantalum precipitate is of a fine, sulfur-yellow color, not light brown as stated in a number of textbooks; discoloration indicates impurities (titanium, iron). The columbium precipitate is more voluminous than the preceding, and has a vivid vermilion color.

(*f*) The tartaro- complexes of the earth acids are not precipitated by ammonia, but boiling with a large excess of hydrochloric or nitric acid causes almost quantitative precipitation of hydrated earth acid. The oxalo- complexes, on the other hand, are precipitated by ammonia, but incompletely by mineral acids.

(*g*) Pertantalic and percolumbic acids are formed when the bisulfate melt (see p. 588, *b*) is treated with a mixture of hydrogen peroxide and dilute sulfuric acid. The melt dissolves to a colorless solution (difference from titanium).

(*h*) The pentafluorides form crystalline double salts with potassium fluoride. Prior to the analytical application of tannin, these were of paramount importance in earth-acid analysis, being the only — though far from perfect — means by which separation of tantalum from columbium could be accomplished. When a tantalum fluoride solution is evaporated with a suitable proportion of potassium fluoride, potassium fluorotantalate, K_2TaF_7, is deposited in the form of difficultly soluble, fine, white needles. The corresponding columbium compound is much more soluble; if a high acidity of the solution is avoided, the double salt hydrolyzes, forming readily soluble oxyfluorocolumbate:

$$K_2CbF_7 + 2\,H_2O \rightleftarrows K_2CbOF_5 \cdot H_2O + 2\,HF$$

This salt is deposited from concentrated solutions in the form of tabular crystals, soluble in 12 to 13 parts of water. Potassium fluorotantalate is soluble in about 200 parts of water at 15°.

Reactions Common to Tantalum and Columbium

1. **Acids.** — Fuse the powdered mineral or oxide (0.1 g) with potassium carbonate (1 g) in a platinum crucible over a Méker burner, and dissolve the melt in 5 ml of *N* potassium hydroxide. The solution, filtered if necessary, gives with mineral acids a white, flocculent precipitate, insoluble in excess, but readily soluble in hydrofluoric acid. This reaction is not specific, being given by certain other metallic acids such as tungstic, stannic, and antimonic (see, however, Reactions 4 and 7).

2. **Potassium Fluoride.** — If the solution of the earth-acid precipitate in hydrofluoric acid (see 1) is treated with 0.1 g of potassium fluoride (or carbonate, which reacts with some of the hydrofluoric acid present) in a small platinum or gold dish, evaporated till crystals begin to separate, and cooled, a crystalline, colorless precipitate of potassium

fluorotantalate, K_2TaF_7, is formed. The crystals are needle-shaped; they may be dried between filter paper and viewed with a strong lens or under the microscope; they consist of acicular orthorhombic prisms.

The reaction is not a very sensitive one, hence it is not suitable for minute quantities of tantalum. Columbium does not react under the above conditions, for the double fluoride remains dissolved in the mother liquor.

3. **Sodium Chloride.** — The alkaline solution, prepared as under 1, when saturated with solid sodium chloride, gives a white crystalline precipitate:

$$K_8Ta_6O_{19} + 8\ NaCl \rightarrow \mathbf{Na_8Ta_6O_{19}} + 8\ KCl$$

$$2\ K_8Cb_6O_{19} + 14\ NaCl + H_2O \rightarrow \mathbf{Na_{14}Cb_{12}O_{37}} + 14\ KCl + 2\ KOH$$

This is a specific earth-acid reaction if it be kept in mind that antimonic acid gives a similar precipitate. The sodium antimonate precipitate, however, gives orange-red antimony sulfide when its solution in hydrochloric and tartaric acids is treated with hydrogen sulfide, but the tartrate solution of the earth-acid precipitate is not affected by hydrogen sulfide.

4. **Tannin Solution.** — (*a*) Treat the suspension of the white flocculent precipitate produced under (§ 2) with 5 ml of fresh 2 per cent tannin solution. The precipitate turns pale yellow.

(*b*) Dissolve the bisulfate melt (see Reaction 2) by heating with 50 ml of saturated ammonium oxalate solution, and treat the resulting solution with tannin reagent as under (*a*). A sulfur-yellow, flocculent precipitate or coloration is produced. If the latter, add 0.5 *N* ammonia drop by drop to the boiling solution till flocculation sets in; the precipitate formed is sulfur-yellow.

5. **Tartaric Hydrolysis.*** — Fuse the powdered mineral or oxide (0.1 g) with potassium bisulfate (2 g) in a silica crucible, and dissolve the melt in a hot solution of tartaric acid (3 g) in 10 ml of water; the tartaric acid reagent may also be applied after conversion into ammoniacal tartrate solution. Filter the solution obtained, if necessary, and boil it with one-third its bulk of strong hydrochloric acid. A white flocculent precipitate, appearing either at once or after some minutes' boiling, proves the presence of earth acid.

The reaction is specific for tantalum and columbium. Tungstic acid also is precipitated under the above conditions, but the precipitate is yellow and is obtained only from concentrated solution, and the precipi-

* Schoeller, *Analyst*, **54**, 456 (1929).

tation is incomplete. The test is not affected by titanium; if zirconium is believed to predominate in the material, this should first be treated by the pyrosulfate-tannin procedure (Reaction 11, p. 550) and the residue from that operation ignited, fused with bisulfate, and submitted to the tartaric hydrolysis reaction.

Specific Columbium Reactions

6. **Tannin Solution.** — (*a*) Treat the suspension of the white, flocculent precipitate produced under 1 with tannin reagent as described under 4. The precipitate turns orange-red.

(*b*) Treat the hot oxalate solution of the bisulfate melt with tannin reagent exactly as described under 4 (*b*). On neutralizing with 0.5 *N* ammonia or with excess ammonium acetate solution, a voluminous flocculent vermilion-red precipitate is produced.

This reaction is not absolutely specific for columbium, because titanium dioxide, after fusing with alkali bisulfate, dissolving in ammonium oxalate, and neutralizing, yields an almost identical precipitate. Titanium oxide, however, does not conform to tests 1 and 7, is not soluble in molten potassium carbonate, and does not give the red tannin precipitate in a solution containing free mineral acid, as is characteristic of columbium. Moreover, titanium in oxalate solution gives with hydrogen peroxide an intense yellow to orange coloration whereas the corresponding columbium solution remains colorless.

7. **Zinc in the Presence of Acid.** — (*a*) If the aqueous extract of the melt obtained by fusing with potassium carbonate (see under 1) is made acid with 7 ml of concentrated sulfuric acid and the solution is evaporated until the precipitated earth acid has redissolved and then, after diluting with 15 ml of water, the liquid is boiled with 1 g of zinc dust, the solution turns brown to ink-black, according to the quantity of columbium present.* Tantalum does not react under these conditions.

(*b*) If a residue of earth acid is dissolved in a platinum dish with a little hydrofluoric acid, a little sulfuric acid is added, and the mixture is heated until dense fumes of sulfuric anhydride are evolved, then, after cooling and adding a little hydrochloric acid and some zinc to the cold solution, the formation of a blue color, due to $CbCl_3$, indicates the presence of columbium. If the reduced solution and hydrofluoric acid is run through a column of amalgamated zinc (Jones' reductor) into a solution of mercuric chloride, a white precipitate of mercurous chloride will be formed.

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* Giles, *Chem. News*, **95**, 1 (1907).

Simultaneous Detection of Tantalum and Columbium

The test here described has the great advantage of utilizing color reactions. It is based on the fact that tantalic acid is precipitated more readily by tannin than columbic acid.*

8. **Titanium is Absent.** — Fuse the mixed oxides (0.05 to 0.2 g) with potassium bisulfate and dissolve the melt by boiling with 50 ml of ammonium oxalate solution (as in Reactions 5 and 8). Test a little of the solution with hydrogen peroxide to make sure that titanium is absent. Boil the remainder of the solution and treat with 0.2 to 0.3 g of tannin followed by 0.5 *N* ammonia drop by drop, if necessary, till a flocculent precipitate is formed. If this is pale to bright yellow, the presence of tantalum is indicated; if orange to red, columbium is present, with tantalum either absent or subordinate. If orange to red, filter off the precipitate, wash it with water, rinse back into the original vessel, boil with 25 ml of saturated ammonium oxalate solution, and dissolve by gradual addition of *N* sulfuric acid. When the solution has cleared, add 0.1 to 0.2 g of tannin, continue boiling, and add 0.5 *N* ammonia, drop by drop, until a precipitate again separates. This will now be yellow if the amount of tantalic oxide present is not too small; if again orange, the precipitate should be filtered off, and the treatment repeated once more. By a refined procedure along these lines, traces of tantalum in columbic oxide can be detected and determined.†

In the presence of much tantalum, columbium is readily detected in the filtrate from the yellow tannin precipitate. The liquid is boiled and treated with more tannin and an excess of ammonium acetate; the columbium is precipitated as the red tannin adsorption complex.

9. **Titanium is Present.** — Fuse the mixed oxides with potassium bisulfate in a silica crucible and extract the melt with a 1 per cent solution of tannin in 5 per cent sulfuric acid, as directed on page 551 (titanium, Reaction 11). Collect the residue from the extraction, wash it with 2 per cent sulfuric acid, ignite, fuse again with bisulfate, and dissolve this melt in hot, concentrated tartaric acid solution. Boil the resulting solution with one-third its bulk of concentrated hydrochloric acid (Reaction 5). This precipitation, while serving as a confirmatory earth-acid reaction, provides for an additional purification from titania. Filter off the hydrolysis precipitate, wash, ignite, and treat by Reaction 8.

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* Powell and Schoeller, *Analyst*, **50**, 494 (1925).

† For a description of this procedure, see *Analyst*, **50**, 496 (1925). The investigations of Schoeller, Powell, and collaborators into the analytical chemistry of tantalum and columbium are recorded in the *Analyst*, Vols. 47, 49, and succeeding volumes.

Reactions in the Dry Way

In the reducing flame, columbic oxide colors the salt of phosphorus bead blue, violet, or brown, according to the amount present; the bead becomes red on addition of ferrous sulfate. Tantalic oxide does not color the bead under any conditions. The oxides of tantalum and columbium are infusible.

ALKALINE EARTH GROUP

RADIUM, Ra. At. Wt. 226.05, At. No. 88

Radium, in its reactions, is very much like barium. Inasmuch as its importance is due to its physical properties, and physical methods serve to detect very small quantities, the identification of this element is the work of the physicist rather than the chemist.

THE ALKALI GROUP

CESIUM, RUBIDIUM, LITHIUM

CESIUM, Cs. At. Wt. 132.91, At. No. 55

Density 1.87. M. P. 26.5°. B. P. 670°

Occurrence. — Cesium and rubidium are not rare elements, strictly speaking, for they are found almost everywhere, but always only in very small amounts. Thus cesium replaces potassium in many feldspars and micas, and is found in many rocks which carry these minerals, as well as in mineral waters which ooze from them. Cesium and rubidium were discovered in the mother liquor of Durkheimer brine in the year 1860 by Bunsen and Kirchhoff by means of the spectroscope. Its name is from the Latin *caesius* = sky blue.

Pollucite, a mineral closely related to leucite, found at Elba and crystallizing in the regular system, is a typical cesium mineral. Its composition is $H_2Cs_4Al_4(SiO_3)_9$.

Properties. — The element cesium is a silvery white, ductile, and soft metal; its density is 1.87. It melts on exposure to the air and ultimately takes fire with a reddish violet flame. It also takes fire when thrown on water. It is the most electropositive of all metals.

Cesium and rubidium in all their reactions behave almost exactly like potassium. The principal difference between these three metals lies in the different solubilities of their corresponding salts.

Cesium Carbonate, unlike the other alkali carbonates, is quite soluble in alcohol.

Reactions in the Wet Way

A solution of cesium chloride should be used

1. $Bi(NO_3)_3$ and $NaNO_2$ precipitate a yellow double nitrite:

$$Bi^{+++} + Na^+ + 2\ Cs^+ + 6\ NO_2^- \rightarrow Cs_2NaBi(NO_2)_6$$

The precipitation is best effected by using a very small volume of cesium solution,

adding one-sixth as much 4 *N* $Bi(NO_3)_3$ solution in 6 *N* acetic acid, and allowing to stand at least fifteen minutes in ice water. In this way 1 mg of rubidium or cesium can be separated from 100 mg of potassium.

2. **Chloroplumbic acid,** H_2PbCl_6, precipitates Cs_2PbCl_6.

The reagent is prepared by passing chlorine gas into a saturated solution of $PbCl_2$ in concentrated HCl. By treating the dry chlorides with 4 ml of concentrated hydrochloric acid and 2 ml of reagent, practically all the cesium and rubidium will be precipitated and 50 mg of potassium will remain in solution. Before the bismuthinitrite method was available, this was probably the best way to separate potassium from rubidium and cesium.

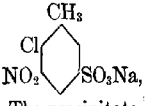
3. $H_2[PtCl_6]$ produces a yellow, crystalline precipitate which is of a lighter color than the corresponding potassium salt and is much less soluble; 100 ml of water dissolves at 0° only 0.024 g, and at 100° 0.377 g, of the salt.

4. H_3SbCl_6, a solution of antimony trichloride in 6-normal HCl, precipitates white cesium chlorantimonite:

$$3\ Cs^+ + SbCl_6^{---} \rightarrow Cs_3SbCl_6$$

By adding 10 drops of the reagent (137 g $SbCl_3$ in 100 ml of 6 *N* HCl) to 3 ml of Rb and Cs ions in 6 *N* HCl, all but about 5 mg of Cs will be precipitated while at least 100 mg of Rb will stay in solution.

5. $H_2[SnCl_6]$ (a solution of $SnCl_4$ in concentrated HCl) produces in concentrated solutions a white, crystalline precipitate of cesium chlorostannate, $Cs_2[SnCl_6]$ (octahedrons). Ammonium salts give the same reaction, but potassium and rubidium salts do not.

6. **Sodium 6-chloro-5-nitrotoluenemetasulfonate,**  , precipitates white cesium chloronitrotoluenesulfonate. The precipitate, however, is much more soluble than the corresponding rubidium salt.

7. **Sodium Cobaltinitrite,** $Na_3Co(NO_2)_6$, produces a yellow precipitate, $Cs_2NaCo(NO_2)_6$. This, and the corresponding precipitates containing Rb or K in place of Cs, are much less soluble in water than the perchlorates. By gentle ignition a mixture of insoluble Co_3O_4 and easily soluble alkali nitrite is obtained:

$$3\ Cs_2NaCo(NO_2)_6 \rightarrow 6\ CsNO_2 + 3\ NaNO_2 + Co_3O_4 + 4\ NO\uparrow + 5\ NO_2\uparrow$$

8. **Silicotungstic Acid,** $H_8SiO_6 \cdot 12WO_3$, precipitates white $Cs_8SiW_{12}O_{42}$. The precipitate is obtained with as little as 0.5 mg of Cs but 8 mg of Rb will remain in solution. Other alkalies or alkaline earths do not interfere with this test.

9. **Tartaric Acid** produces, as with potassium and rubidium, a white, crystalline precipitate, $CsHC_4H_4O_6$, in concentrated solutions; 100 ml of water dissolves at 25° 9.7 g and at 100° 97.1 g of the salt.

Reactions in the Dry Way

Cesium compounds color the flame reddish violet, very similar to the potassium flame.

Flame Spectrum. — An intensely blue double line, **455.5** mμ, **459.3** mμ. At higher temperatures a number of paler lines appear of subordinate importance; in the red 697.3 mμ and 672.3 mμ, in the orange-yellow 621.3 mμ and 601 mμ, in the yellow 584.5 mμ, in the green 566.4 mμ, 563.5 mμ, 550.3 mμ, 547.1 mμ, 541.9 mμ, and 535.1 mμ. Moreover, a faint continuous spectrum is seen from the yellow to the blue.

RUBIDIUM, Rb. At. Wt. 85.48, At. No. 37

Density 1.52. M. P. 38°. B. P. 700°

Occurrence. — Rubidium almost always accompanies cesium and is found in many mineral waters; in carnallite from Stassfurt; in lepidolite, $(Li,K,Na)_2Al_2(F,OH)_2Si_2O_5$; in triphyllite, $(Fe,Mn)(Li,Cs,Rb)PO_4$; and in spodumene, $(Li,Na)Al(SiO_3)_2$, a mineral of the pyroxene group. Lepidolite from Rozena contains about 0.54 per cent Rb and 0.0014 per cent Cs. Rubidium salt has been found in beet-root molasses. The name *rubidium* is from the Latin *rubidus* = red.

Next to cesium, it is the most electropositive metal.

Reactions in the Wet Way

1. **$Bi(NO_3)_3$** and **$NaNO_2$** precipitate a yellow double salt.

$$Bi^{+++} + 2\,Rb^+ + 6\,NO_2^- + Na^+ \rightarrow Bi(NO_2)_3 \cdot 2\,RbNO_2 \cdot NaNO_2$$

2. **$H_2[PtCl_6]$** produces, as with cesium and potassium salts, a yellow, crystalline precipitate of $Rb_2[PtCl_6]$, which is more difficultly soluble than the corresponding potassium salt, but more soluble than the cesium salt; 100 parts of water dissolve at 0° 0.134 part, and at 100° 0.634 part, of the salt.

3. **H_3SbCl_6**, **$Na_3Co(NO_2)_6$**, **$H_8SiO_5 \cdot 12\,WO_2$**, **H_2PbCl_6**, and **$C_7H_5ClNO_2SO_2Na$** precipitate rubidium salts as with cesium (see above). It is impossible to effect a complete separation of rubidium and cesium by means of a single precipitation with any one reagent. Rubidium acid tartrate and rubidium chloronitrotoluenesulfonate are much less soluble than the corresponding cesium compounds while cesium chlorantimonite and cesium silicotungstate are less soluble than the corresponding rubidium salts. By treating a concentrated solution of alkali salts first with H_3SbCl_6 any cesium in excess of 5 mg will be precipitated and at least 100 mg of rubidium will remain in solution. Then, if the Cs_3SbCl_6 precipitate is removed, the solution can

be tested for rubidium with sodium acid tartrate or, better still, with chloronitrotoluenesulfonate without interference from the small quantity of cesium remaining in the solution.

4. $H_2[SnCl_6]$ produces a white precipitate only in very concentrated solutions. The salt is much more soluble than the corresponding cesium salt, but this reaction is not suitable for separating the two metals.*

5. **Tartaric Acid** produces a precipitate of $RbHC_4H_4O_6$ only in concentrated solutions; 100 parts of water dissolve at 25° 1.18 parts, and at 100° 94.1 parts, of the salt. The corresponding cesium salt is more soluble; that of potassium is less soluble.

Reactions in the Dry Way

Flame Coloration. — Similar to cesium.

Flame Spectrum. — Violet double lines **420.2** mμ and **421.5** mμ, also the red double line 781.1 mμ and 795.0 mμ. At higher temperatures a continuous spectrum is visible from the yellow to the blue in which the following lines are to be found in addition to those given above: in the orange-yellow 629.8 mμ, 626.1 mμ, 620.6 mμ, 617.7 mμ; in the yellow-green 572.4 mμ, 570.0 mμ, 564.8 mμ; and of subordinate importance the green lines 543.5 mμ, 536.5 mμ, and 516.8 mμ.

SEPARATION OF POTASSIUM AND RUBIDIUM FROM CESIUM

Method of Stolba

To the concentrated solution of alkali salts, add a solution of antimony trichloride in concentrated hydrochloric acid which causes the prompt precipitation of cesium chlorantimonite. Filter and wash with concentrated hydrochloric acid, using a hardened filter paper.

LITHIUM, Li. At. Wt. 6.94, At. No. 3

Density 0.534. M. P. 186° B. P. 1400°

Occurrence. — Lithium is found to a greater extent in nature than cesium and rubidium; in triphyllite, $(Fe,Mn)(Li,Cs,Rb)PO_4$; in petalite, $Al(Li,Na,H)Si_4O_{10}$, a mineral of the feldspar group (also called castorite); in amblygonite, $Li(AlF)PO_4$, monoclinic; in lepidolite, $Al_2(Li,K,Na)_2(F,OH)_2Si_2O_5$; in many varieties of tourmaline, and muscovite, in epidote and orthoclase, and consequently in many mineral-spring waters. In some spring water as much as 36 mg Li is contained in a liter.

Properties. — Lithium is the lightest of all metals, and floats on petroleum. It oxidizes quickly in the air, and decomposes water at ordinary temperatures, forming LiOH, which dissolves slowly in the water; the solution reacts alkaline and absorbs

* Stolba, *Z. anal. Chem.*, **12**, 440, recommends this reaction for separating rubidium and cesium, but Godeffroy, *Ber.*, **7**, 375, and Cossa, *Z. anal. Chem.*, **17**, 350, obtained better results with the chlorantimonite reaction.

carbon dioxide from the air with avidity, forming difficultly soluble Li_2CO_3. The name *lithium* is from the Greek *lithos* = stone.

Metallic lithium costs about $2.50 per lb and is used in some alloys. Thus a Pb-Ca-Li alloy is used as bearing metal and Al-Li ("scleron") is a substitute for brass. Lithium compounds are used in medicine, fireworks, and to some extent in glass making.

Lithium chloride is soluble, even in the anhydrous state, in a mixture of alcohol and ether as well as in amyl alcohol (difference from the remaining metals of this group).

Reactions in the Wet Way

A solution of lithium chloride should be used.

1. **Ammonium Fluoride** in ammoniacal solution slowly precipitates white, gelatinous lithium fluoride:

$$2\ Li^+ + F_2^{--} \rightarrow Li_2F_2$$

One gram of the precipitate requires 3,500 ml of water to dissolve it; the same quantity of sodium fluoride requires only 70 ml of water and the other alkali fluorides are more soluble. Carnot,* therefore, uses the reaction for the separation of lithium from the other alkalies. The reagent should be pure and free from ammonium fluosilicate.

To test for small quantities of lithium ions, evaporate the solution with hydrofluoric acid on the water bath in a platinum dish and treat the residue with a little dilute ammonia.

2. $H_2[PtCl_6]$ produces no precipitation.

3. Na_2HPO_4 precipitates white lithium phosphate in alkaline solutions:

$$HPO_4^- + 3\ Li^+ + OH^- \rightarrow Li_3PO_4 + H_2O$$

If a dry alkali salt is treated with 3 ml of 95 per cent alcohol and 2 drops of concentrated ammonium hydroxide and the resulting solution is filtered if necessary, then on adding 3 ml more of ammonium hydroxide and some Na_2HPO_4 reagent, a precipitate of lithium phosphate will be obtained if 0.1 mg of Li is present. If much more alcohol is added, there is danger of $Na_2NH_4PO_4$ being precipitated. Lithium phosphate is easily melted, whereas phosphates of the alkaline earths and magnesium are not.

4. $(NH_4)_2CO_3$. If ammonium carbonate and ammonia are added to a concentrated lithium solution, lithium carbonate is precipitated in the form of a white powder. The salt, contrary to the other alkali carbonates, is difficultly soluble in water: 100 parts of water dissolve at 13° C 1.31 parts of Li_2CO_3. In the presence of considerable alkali chloride or of ammonium chloride, no precipitation takes place.

5. **Tartaric Acid** produces no precipitation.

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* *Z. anal. Chem.*, **29**, 332.

Reactions in the Dry Way

Flame Coloration. — Pure lithium salts impart a magnificent, carmine-red coloration to the gas flame. If considerable amounts of sodium salts are present, the lithium flame is completely masked; but if the flame is observed through cobalt glass the red color becomes distinctly visible.

Flame Spectrum. — An intensely red line **670.3** mμ and at higher temperatures the pale orange-yellow line 610.3 mμ.

ELEMENT 87, EKACESIUM or VIRGINIUM, Vi

In the periodic classification of the elements (cf. p. 87) element 87 is missing. Considerable evidence has accumulated from spectroscopic studies and the use of the magneto balance that such an element exists. The element has been described as *ekacesium*, but the name *virginium* and symbol Vi have been proposed for it. The element is so rare that its chemical properties have not been studied, but it is reasonable to assume that it is even more basic than cesium and it is to be expected that the virginium salts corresponding to difficultly soluble potassium, rubidium, and cesium salts will be less soluble.

DETECTION OF SODIUM, LITHIUM, POTASSIUM, RUBIDIUM, AND CESIUM *

1. **Removal of NH_4^+.** — Since ammonium salts interfere, it is first necessary to remove them. To accomplish this, evaporate the filtrate from the alkaline earth precipitate to dryness and heat with a moving flame until no more fumes are evolved, avoiding a high temperature for fear of volatilizing alkali salts. Cool; add 5 ml of water and 1 drop of ammonium hydroxide. Filter, and reject any residue.

2. **Removal of SO_4^{--}.** — Sulfate interferes with the analysis of this group because of the slight solubility of Na_2SO_4 and $NaHSO_4$ in alcohol. To the solution add 1–3 ml of concentrated HNO_3 and evaporate to dryness, gently igniting the residue. Cool, add 5–10 ml of water and normal $Pb(NO_3)_2$ solution, a few drops at a time, until there is no further precipitation of $PbSO_4$. Shake and allow to stand for five minutes. Filter, wash the precipitate with a little water, and reject it. Saturate the filtrate with hydrogen sulfide, heat to coagulate the precipitate, filter, and reject the precipitate of PbS.

3. **Removal of K, Rb, and Cs.** — To the solution in a 25-ml casserole, add 1–5 ml of 9 *N* $HClO_4$ and evaporate cautiously till fumes of $HClO_4$ are evolved freely. Enough of the reagent must be added to combine with all the alkali ions present, and the heating should continue till all HNO_3 is volatilized. Let the liquid cool completely, and when cold rinse it into a small, dry flask using 4 times as much 99 per cent alcohol as there was used of $HClO_4$. (If the alcohol is added to *hot* $HClO_4$ there is likely to be a dangerous explosion.) Cool the mixture in the flask, shake well, and allow to stand fifteen minutes. Filter through a small, *dry* filter into a dry flask. Wash the precipitate with 2 ml of 99 per cent alcohol. It will contain all the K, Rb, and Cs as perchlorates. The filtrate contains soluble perchlorates of Li and Na.

* The procedure here given is that by Noyes and Bray, *Qualitative Analysis for the Rare Elements*. It assumes that other cations have been removed by the usual qualitative procedure.

4. **Separation of Li and Na.** — Saturate the alcoholic solution with dry HCl gas, keeping the flask surrounded by ice water and using narrow glass tubing for introducing the gas. Introduce the gas until fumes of HCl escape from the alcoholic solution. Let the solution stand thirty minutes, and filter through a small, dry filter. Wash the precipitate with not more than 5 ml of 99 per cent alcohol which has been saturated with dry HCl. At once add to the filtrate one-fourth of its volume of water, which helps decompose any $C_2H_5ClO_4$ formed, and lessens the danger of explosion during the subsequent evaporation. The above treatment serves to precipitate as little as 0.5 mg of Na as NaCl while as much as 100 mg of Li remains in solution as LiCl.

5. **Confirmatory Test for Na.** — Dissolve the NaCl precipitate by pouring 5 ml of water through the filter several times. To the solution add 1 ml of 95 per cent alcohol and 5 ml of magnesium uranyl acetate reagent. As little as 0.5 mg of Na gives a distinct precipitate of $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 9\ H_2O$ almost immediately, but 10 mg of K, Rb, Cs, or Ca gives no precipitation. Two milligrams of Li give no precipitate, but with 5–10 mg of Li a precipitate forms after a few minutes and then gradually increases. If the precipitate is very small, the flame test will show whether it is NaCl or LiCl.

6. **Detection of Li.** — Evaporate the alcoholic solution obtained as described in § 4 *on a steam-bath* (a free flame is very likely to cause a violent explosion) until the volume is reduced to that of the $HClO_4$ used in § 3. Cool to room temperature and add concentrated nitric acid, very slowly, a drop at a time, until there is no further action. This is added to oxidize the alcohol which has not been removed by evaporation. It is essential that all alcohol should be removed before the perchloric acid is heated above 100°. Add 1 ml of concentrated nitric acid in excess and heat *on a steam-bath* for fifteen minutes. Then add 1 ml more of concentrated nitric acid and heat the dish over a wire gauze until all the $HClO_4$ is volatilized. (If these directions are carried out carefully there should be no explosion, but it is best to operate in such a way that an explosion will not harm anyone.) Finally heat the dish for a minute or two over a free flame to a temperature below redness. Cool; add 3 ml of 95 per cent alcohol and 2 drops of concentrated NH_4OH. Filter, and reject any residue. To the solution add 3 ml of concentrated NH_4OH, heat to 35–40°, and add 2 drops of 0.5 *N* Na_2HPO_4 solution. Shake to dissolve any local precipitate of Na_2HPO_4. If a precipitate of Li_3PO_4 forms, add 2 ml of water and more Na_2HPO_4 until no further precipitation takes place. As little as 0.1 mg of Li gives a noticeable precipitate of Li_3PO_4.

7. **Conversion of $KClO_4$, $RbClO_4$, and $CsClO_4$ to Nitrites.** — For the subsequent separation it is necessary that the alkali metals should be in the form of readily soluble salts, preferably the nitrites. To accomplish this the perchlorates are changed to less soluble cobaltinitrites and these are decomposed by ignition, whereby alkali nitrite and insoluble Co_2O_4 are formed. Transfer the $HClO_4$ precipitate, obtained as described in § 4, to a casserole by dissolving it on the filter with a little hot water. Evaporate to dryness, and to the residue add 3–12 ml of molar $Na_3Co(NO_2)_6$ reagent which has been mixed with half as much 6 *N* acetic acid. Let stand ten to fifteen minutes with frequent stirring, and filter off any precipitate of $K_2NaCo(NO_2)_6$, $Rb_2NaCo(NO_2)_6$, or $Cs_2NaCo(NO_2)_6$. Wash the precipitate with 5–10 ml of the reagent diluted with 10 volumes of water. Reject the filtrate. Transfer the precipitate to a 25-ml casserole, add 1 ml of potassium-free 9 *N* $NaNO_2$ solution, evaporate to dryness, and ignite the residue gently until it fuses and no longer effervesces. Cool, add 5–10 ml of water, filter, and reject the black residue of Co_3O_4. Evaporate just to

dryness; add 1–2 ml of water and 6 *N* acetic acid until the solution is barely acid to litmus. Filter if necessary, and reject the residue.

8. **Separation of Rb and Cs from K.** — The separation to be described depends upon the fact that Rb and Cs react with $NaNO_2$ and $Bi(NO_3)_3$ to form slightly soluble salts, $Rb_2NaBi(NO_2)_6$ and $Cs_2NaBi(NO_2)_6$. To make the separation as complete as possible the solution should have a small volume, and contain considerable $NaNO_3$ with relatively little $Bi(NO_3)_3$. To the nitrite solution in a small test tube add one-sixth of its volume of $Bi(NO_3)_3$ reagent, shake until any local precipitate dissolves, stopper the tube, and let it stand fifteen to thirty minutes in ice water. Then warm to 30° and stir frequently for five minutes or longer. (Yellow, crystalline precipitate shows presence of Rb or Cs.) If a large precipitate forms, add 0.5-ml portions of both $Bi(NO_3)_3$ and $NaNO_2$ reagents and let stand another thirty minutes in ice water. Filter through a small, dry filter, and wash with not more than 2 ml of an ice-cold mixture of 9 *N* $NaNO_2$ mixed with one-fourth as much $Bi(NO_3)_3$ reagent. The above treatment serves to separate 1 mg of either Rb or Cs from 500 mg of K.

9. **Detection of K.** — To the filtrate from the bismuthinitrite precipitate, add, from a dropper, 1 drop of 0.3 *N* $Co(NO_2)_2$ solution and heat to 35° for ten minutes. This serves to precipitate any Rb that escaped precipitation as complex nitrite. Cool in ice water, let stand one hour, filter, and reject the precipitate. To the filtrate add 0.5 ml of 6 *N* acetic acid, 2 ml of water, and 0.2–2 ml of 3 *N* $Co(NO_2)_2$ solution. Let the mixture stand at least thirty minutes. A yellow precipitate of $K_2NaCo(NO_2)_6$ will be obtained if 1 mg of potassium is present. This quantity of potassium will precipitate, to be sure, upon the first addition of Co to the nitrite solution, but enough will remain in solution to give a test after the removal of the Rb.

10. **Partial Separation of Cs from Rb.** — The following procedure serves to precipitate any Cs in excess of 5 mg, and 100 mg of Rb will remain in solution. Dissolve the bismuthinitrite precipitate (§ 8) in 3 ml of 6 *N* HCl, boil a few minutes to expel oxides of nitrogen, cool, add 10 drops of 6-molar $SbCl_3$ reagent, and let stand thirty minutes with frequent stirring. A white, crystalline precipitate of $Cs_3Sb_2Cl_9$ will form if more than 5 mg of Cs is present. Filter through a small filter and reject the precipitate.

11. **Final Separation of Rb from Cs.** — To the filtrate from the $Cs_3Sb_2Cl_9$ precipitate, add 15 ml of water and saturate with H_2S to remove Sb and Bi. Filter and reject the Sb_2S_3 and Bi_2S_3 precipitate. Evaporate the filtrate to dryness, add 2 ml of water, again saturate with H_2S, and pour the solution through a small filter into a short Pyrex test tube. Evaporate the solution carefully to dryness, cool, and add 5 drops of saturated sodium acid tartrate solution (or, better, 1 ml of a saturated solution of sodium chloronitrotoluenemetasulfonate). Stir frequently for at least five minutes, then add 5 ml more of the tartrate reagent and let stand ten minutes. A white, crystalline precipitate of $RbHC_4H_4O_6$ is obtained with 1 mg of Rb; Cs does not give a precipitate unless 10 mg is present. Potassium reacts with both reagents to give precipitates like Rb.

12. **Final Test for Rb.** — Through the filter containing the $RbHC_4H_4O_6$ precipitate, pour 0.5–5 ml of 9 *N* $NaNO_2$ solution, add 3–30 drops of $Bi(NO_3)_3$ reagent, shake, and let stand thirty minutes in ice water. A yellow precipitate at this stage is $Rb_2NaBi(NO_2)_6$.

13. **Final Test for Cs.** — To the filtrate from the $RbHC_4H_4O_6$ precipitate add 3 ml of molal silicotungstate reagent and let the mixture stand at least thirty minutes. A fine white precipitate of $Cs_8SiW_{12}O_{42}$ denotes Cs, but it must be remembered that all Cs over about 5 mg was precipitated as $Cs_3Sb_2Cl_9$ (§ 10).

For the detection of small quantities of alkali metals, the spectroscope is invaluable. From silicates, the alkali salts can be obtained as outlined on page 448, method 3.

RHENIUM, Re. At. Wt. 186.31, At. No. 75

Density about 21.2. M.P. > 3100°

Among the elements lately discovered, none is more interesting than rhenium which was detected by the study of x-ray spectra by Noddack, Tacke, and Berg in 1924. In the periodic table of Mendeléeff (p. 87) there were three missing elements in Family VII; Mendeléeff predicted that elements would be discovered to fill these gaps and prophesied what the properties of these elements would be. He called element 43 *eka-manganese* and element 75, *dvi-manganese*.

Rhenium, which is named after the German *Rhine*, corresponds to dvi-manganese. *Masurium*, Ma, also discovered by Noddack and his co-workers, corresponds to eka-manganese. Concerning masurium, little is known, although lines have been detected in the x-ray spectra which are probably caused by the presence of very small quantities of this element in rare minerals such as columbite, sperrylite, etc. Another member of Family VII of the periodic table is element 85. This element belongs to the other side of the family and should be the analogue of iodine; it has been called *eka-iodine*. Allison and Murphy believe that they have detected this element and have studied its properties by magneto-optical analysis. To it they have assigned the name *alabamine*, Am, and the atomic weight 221.

Rhenium has been detected in at least 100 minerals, but the maximum concentration found was about 0.001 per cent Re. The facts that it forms a sulfide Re_2S_7, which is insoluble in acid, and that this sulfide can be changed to the oxide Re_2O_7 which is quite volatile, have made it possible to recover appreciable quantities of rhenium oxide from minerals containing very little rhenium. By reduction of the oxide in hydrogen, the metal itself has been obtained as a heavy, gray powder. Metallic rhenium resembles platinum in appearance and, next to tungsten, is the hardest to melt of all metals. It is possible to purchase rhenium, or its perrhenate, $KReO_4$, at about $4 per gram of Re. Rhenium is easily dissolved by nitric acid, but instead of getting $Re(NO_3)_2$, as might be expected, $HReO_4$ is formed:

$$3\ Re + 7\ NO_3^- + 7\ H^+ \rightarrow 3\ HReO_4 + 7\ NO + 2\ H_2O$$

It dissolves slowly in sulfuric acid but is not attacked by HCl or HF.

At least five oxides of rhenium have been described. Black rhenium dioxide, ReO_2, corresponds in its composition to MnO_2. It has been obtained by adding KI to the concentrated hydrochloric acid solution of $KReO_4$ and neutralizing with NaOH. Under similar conditions, manganese would give $MnCl_2$ and a precipitate of $Mn(OH)_2$. ReO_2 has also been obtained by adding considerable hydrazine hydrochloride, $N_2H_4 \cdot 2\ HCl$, to a solution of perrhenate in 50 per cent KOH.

Rhenium trioxide, ReO_3, has been described as a red powder, and intermediate oxides such as Re_2O_5, of violet or blue colors, have been mentioned.

Yellow rhenium heptoxide, Re_2O_7, is obtained easily by heating Re in the air or in oxygen above 150°. It melts at 220° and sublimes at a somewhat lower temperature. White Re_2O_5 is formed when Re or a lower oxide is heated below 150°. It melts at that temperature and changes rapidly into Re_2O_7. These two oxides, Re_2O_7 and Re_2O_5, are acid anhydrides and are readily soluble in water, but the lower oxides are weakly basic. As is true of the manganates, the salts of rhenic acid,

H_2ReO_4, are fairly stable in alkaline solutions but decompose slowly into dioxide and perrhenate:

$$3\ ReO_4^{--} + 2\ H_2O \rightarrow 2\ ReO_4^{-} + ReO_2 + 4\ OH^{-}$$

The perrhenates are less stable in alkaline solutions but are much more stable in acid solutions. Perrhenic acid, $HReO_4$, is a fairly strong acid, much more stable than permanganic acid. It will dissolve hydroxides such as $Al(OH)_3$, liberate CO_2 from carbonates, and dissolve metals with liberation of hydrogen. An aqueous solution of R_2O_3 reacts like a peroxide.

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